Comment on amt-2021-102
Anonymous Referee #2


Development of a Laser-Photofragmentation Laser-Induced Fluorescence instrument for the detection of nitrous acid and hydroxyl radicals in the atmosphere

Bottorff et al., Atmospheric Measurement Techniques Discussions, doi.org/10.5194/amt-2021-102

The authors report the development, characterisation and initial results from a novel instrument designed to detect HONO and OH in the atmosphere. The instrument is based on the fluorescence assay by gas expansion (FAGE) technique used to detect OH radicals in the atmosphere by laser induced fluorescence, which has been developed to provide measurements of HONO by measuring the OH fragment produced following the laser photolysis of HONO.

The manuscript is well presented and provides a detailed description of the instrument, its calibration, and initial results obtained in both outdoor and indoor field measurements. The description of the development and calibration of the instrument are within the scope of the journal, with the field measurements providing an indication of the capabilities of the instrument and as such are relevant to the publication.

There are, however, a number of areas in which the manuscript could be improved prior to publication which are listed below:

Line 26: ‘hydroperoxy’ is generally preferred over ‘hydroperoxyl’.

Line 37: Although likely clear to most readers, the terms in equation 2 ought to be defined for clarity.

Line 40: It may also be worth commenting that the wavelengths at which HONO photolyses to produce OH compared to other OH sources contribute to its role as a significant early morning OH source.

Line 95 onwards: There have been reports of photofragmentation-LIF technique used to measure HONO in laboratory experiments (e.g. Dyson et al., 2021 doi.org/10.5194/acp-21-5755-2021) which should be included in the discussion.
Line 102: The wavelength limit for O(1D) production from ozone photolysis is usually given as 340 nm. Please clarify.

Line 178 (and elsewhere): ‘Criegee intermediates’ is preferred over ‘Criegee radicals’.

Lines 180-183: It is not entirely clear from the description whether this method is used in any of the HONO measurements reported to remove ambient OH. Please clarify.

Line 195: Add the physical state for HONO.

Line 196: What are typical concentrations generated by this method?

Line 199: How would production of CINO result affect the measurement of HONO? Is it a problem for this technique?

Line 201: It’s not clear what the “long warmup times” refer to, what requires warming up with the method described?

Line 221: It might be more appropriate to refer to an effective oxygen absorption cross-section rather than state the absorption cross-section is dependent on operating conditions. The cross-section itself is a fundamental physical property, it is more the measurement of the cross-section that depends on conditions.

Line 242 onwards: Is there any other chemistry that should be considered? Model simulations are referred to in line 250 but no information is provided on the model or mechanism. Some additional details are required on this, and it may be appropriate to include Figure S4 in the main text.

Lines 258 and 271: Can the authors comment on the identities and possible concentrations of the impurities in the NO leading to the production of OH or reduction in apparent photofragmentation efficiency? Could the same species result in interferences in ambient measurements? See also comment below. Are scrubbers to remove NO used in the calibrations described in this work?

Line 285: Are there any measurements to show how much (or how little) the photofragmentation efficiency varies throughout a prolonged measurement period? A table summarising detection limits, photofragmentation efficiencies, uncertainties, conditions etc. for calibration experiments and the measurements reported in sections 3.1 and 3.2 would be useful.

Line 306: What is the estimate based on?

Line 380 onwards: The manuscript would benefit from a more detailed description of potential interferences. Previous work by Liao et al. is referenced, but a more complete discussion of this work and its relevance to the current work is required. It would help to show some model calculations of species that may photolyse at 355 nm and lead to OH signals to demonstrate the impact of potential interferences. HOCl is mentioned as a potential problem during the indoor measurements, it would help if the authors could present some model calculations to indicate whether this is likely only a problem for indoor measurements, or whether ambient concentrations of HOCl could be problematic in outdoor field measurements. Similarly, are there any potential issues relating to HOB or HOI in marine environments? Are there are other species which might significantly impact the measurement through production of OH or a reduction in the effective photofragmentation efficiency? Does absorption of the 355 nm light by other ambient species, such as formaldehyde, cause any potential interference by reducing the effective photofragmentation efficiency of HONO?
Line 412 onwards: The conclusions section reads more as a section on future work. It would help to include a summary of the operating conditions and measurement capabilities.

Figure 3: The image quality may need to be improved prior to final publication.

Figure 4: Can the authors clarify what is meant by ‘S1,3’, is this the average of S1 and S3?

Figure 5: Can the symbols be matched to those given in Figure 4?

Figure S1: Please clarify whether the laser used to photolyse HONO was a Nd:YAG (355 nm third harmonic) or Nd:YLF (351 nm third harmonic).

Figure S2: A schematic diagram may be more helpful than the figure provided.