We would like to thank the reviewers for their efforts in reviewing this manuscript, and we feel that the manuscript is much stronger with their suggested changes. Below are detailed responses to their comments, which are highlighted in italics.

Reviewer #1

The authors aim for describing a new instrument for the detection of HONO by laser-photofragmentation of HONO and subsequent detection of OH by LIF. Although the topic of the paper would have been in the scope of this journal, the way the authors structure the paper is not appropriate. The authors give an adequate clear description of the instrument and its calibration.

However, the results and discussion part is not fitting the scope of the journal. The authors mainly describe measurements and try to give a chemical explanation of the observed concentrations. This is clearly out of the scope of this journal and should be significantly shortened. Unfortunately, the authors give only little results and discussion of the performance of the instrument. Even the discussion of interferences is kept on a level of estimates from literature and the only experimental result is only mentioned to be discussed in future publications. More detailed experimental investigations in the laboratory could have been done.

A comparison of the measured HONO/OH ratio with calculations could have been valuable, if this is used to test the validity of the instrument. However, this is likely not possible, because concentrations are not only determined by the photo-stationary state of gas-phase reactions and the additional measurements may be incomplete or not of high-enough quality. Another option would have been to include a detailed comparison with the CIMS instrument, but the author decided not to do so, but to shift this to another publication.

Overall, the authors mention topics that could have been discussed to show and discuss the performance of the instruments even without further experiments, which would have been even better. Because of the lack of content, I recommend rejecting the paper. It might become suitable for the journal, if there is a broader discussion of results.

As suggested, we have included a few examples of the intercomparison with the University of Toronto CIMS instrument during the HOMEChem campaign, illustrating the excellent agreement between the instruments, and we have expanded the discussion of potential interferences. We have included two examples of the intercomparison in Figure 9 of the revised manuscript. The first example illustrates the agreement between the instruments during a cooking episode, and is discussed on pages 11-12 of the revised manuscript:

Figure 9 illustrates an example of the LP/LIF measurements and the University of Toronto CIMS instrument (Collins et al., 2018) during a cooking event using a gas stove during HOMEChem. During this experiment, mixing ratios of HONO were approximately 2 ppb for several hours prior to the cooking episode. When the gas stove was turned on, mixing ratios of HONO quickly increased to approximately 6 ppb before slowly decaying after the gas stove was turned off. As illustrated in this figure, the LP/LIF measurements of HONO were in excellent agreement with the CIMS measurements during this event, with the measurements agreeing to less than 20%, and are representative of the overall agreement during the intercomparison, which will be presented in a future publication. These results provide confidence in the accuracy of the LP/LIF instrument and the calibration method.
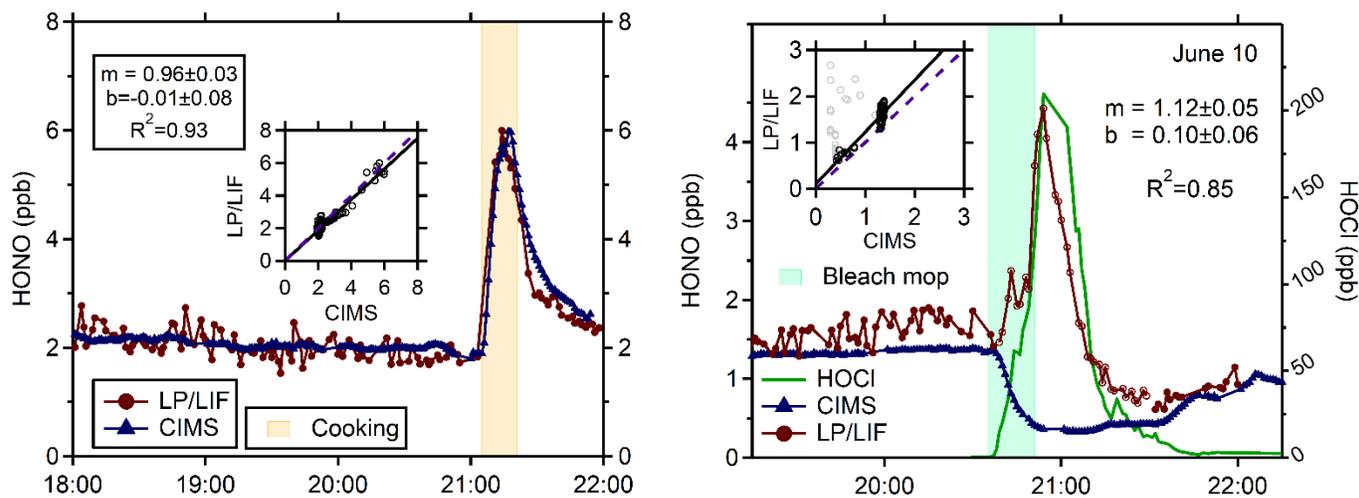
Figure 9: Measurements of HONO by the LP/LIF instrument (red points) and the University of Toronto CIMS instrument (blue points) from a cooking experiment (left) and a bleach mopping experiment (right) during the HOMEChem study illustrating the interference in the LP/LIF instrument from HOCl. The correlation coefficients for the bleach mopping experiment exclude the LP/LIF measurements when HOCl was elevated.

The second example from the intercomparison in Figure 9 illustrates the interference in the LP/LIF instrument from HOCl during a bleach mopping episode, and is discussed as part of the expanded discussion of potential interferences on pages 12-13 of the revised manuscript:

Potential interferences with outdoor measurements of HONO include species that photolyze at 355-nm leading to both prompt and secondary production of OH in the detection cell. Possible prompt interferences include HNO_3, H_2O_2, and other organic peroxides, while potential secondary interferences include species that could produce OH precursors from photolysis, such as HO_2 from the photolysis of HCHO and HO_2NO_2, which could react to produce OH. A previous analysis of the impact of these species on the atmospheric pressure LP/LIF instrument by Liao et al. (2006a) suggested that the photolysis of typical ambient mixing ratios of these species would not lead to the production of significant OH concentrations at a photofragmentation laser pulse energy of approximately 700 mJ at 355-nm, with 1 ppb of HCHO and 1ppb HO_2NO_2 together estimated to produce 0.16 ppt of OH, 1ppb of H2O2 estimated to produce 1.1 ppt of OH, and 1ppb of HNO_3 estimated to produce 0.03 ppt of OH (Liao et al., 2006a). Given that the LP/LIF instrument described here utilized a much lower pulse energy (0.2 mJ) and the mixing ratios of potential interfering species are reduced upon sampling at low pressure, it is likely that any OH produced by photolysis of these species would be significantly less than that estimated by Liao et al. (2006a) and would not significantly interfere with outdoor HONO measurements, and the short time interval between the 355 and 308-nm laser pulses likely minimizes these and other secondary interferences.

During HOMEChem measurements of gas phase organics were generally higher indoors than outdoors across a broad range of species that were further enhanced during cooking events (Farmer et al., 2019). The cooking events likely increased the concentration of formaldehyde, as combustion from gas stoves can be a significant source of formaldehyde, resulting in indoor mixing ratios potentially greater than 10 ppb (Salthammer et al., 2010; Logue et al., 2014). The agreement of the LP/LIF instrument with the CIMS instrument during these events such as that illustrated in Figure 9 suggests that interferences from the photolysis of formaldehyde or the potential reduction of the photofragmentation efficiency due to absorption of the 355 nm laser by formaldehyde are likely minimal. Unfortunately, formaldehyde concentrations were nor quantified during HOMEChem, and additional measurements together with quantification of formaldehyde concentrations will be needed to confirm these results.

However, higher concentrations of other species that photolyze at 355-nm leading to the formation of OH could interfere with measurements of HONO. One possible indoor interference is HOCl, which can be produced during chlorine bleach mopping episodes. Figure 9 also shows a bleach mopping experiment during HOMEChem that resulted in the production of approximately 100-200 ppb of HOCl. During several of these episodes, measurements of HONO by the LP/LIF increased and were correlated with the HOCl measurements, while the HONO measurements by the University of Toronto CIMS instrument decreased as expected during these bleach mopping episodes, as the increase in pH likely impacted the surface equilibrium production of HONO (Collins et al., 2018; Wang et al., 2020b). Although the absorption cross section of HOCl is approximately a factor of 40-50 times lower than that of HONO (1.2×10^{-20} cm^2) (Burkholder et al., 2019) the indoor mixing ratios of HOCl during several of these mopping episodes were 50-100 times greater than the mixing ratios of HONO during these experiments. Bleach mopping experiments that produced lower mixing ratios of HOCl (less than 12 ppb) resulted in lower interferences in the LP/LIF instrument and better agreement with the CIMS instrument. This interference will be examined in a future publication. It appears unlikely that outdoor mixing ratios of HOCl would be a significant interference given that HOCl mixing ratios in marine environments are generally less than 1 ppb (Lawler et al., 2011), much lower than the level of indoor HOCl that produced an interference during HOMEChem. While the absorption cross sections of HOBr and HOI are factors of approximately 10 and 30 times greater than that of HOCl at 355 nm (Burkholder et al., 2019), outdoor ambient mixing ratios of HOBr and HOI are much lower than ambient HOCl, with measured values of HOBr less than 26 ppt in the arctic marine boundary layer (Liao et al., 2012), and measured mixing ratios of HOI less than 70 ppt in the marine boundary layer (Tham et al., 2021). Thus, it is unlikely that outdoor mixing ratios of HOBr and HOI would significantly interfere with LP/LIF measurements of HONO. However, these and other potential interferences, both prompt and secondary, will need to be tested in the laboratory.

We feel that the inclusion of examples of the instrument intercomparision, as well as the expanded discussion of interferences as suggested, better illustrates the performance of the LP/LIF instrument.

Detailed comments to the part of the experimental section:

L13: Full calibration of the sensitivity requires also the calibration of the OH detection sensitivity.

We have clarified that the HONO calibration also requires calibration of the OH detection sensitivity in the abstract of the revised manuscript as suggested.

The LP/LIF instrument is calibrated by determining the photo-fragmentation efficiency of HONO and calibrating the instrument sensitivity for detection of the OH fragment.

L16: Does the LOD refer to HONO and OH?

We have clarified that the LOD refers to the HONO limit of detection in the abstract.

The LP/LIF instrument has demonstrated a 1σ detection limit for HONO of 9 ppt for a 10-min integration time.

L39: The explanation of HONO accumulating during nighttime is a bit misleading, because gas-phase reaction alone would not explain the increase of HONO during the night, but only shift the photo-stationary state to HONO at dawn.

We agree and have removed this statement from the revised manuscript.

L166: Here or somewhere else the authors should mention the duration of each step in the measurement cycle.

We have clarified that the typical duration in each step is 15-s on page 5 of the revised manuscript as suggested.

Each measurement cycle consists of four 15-s steps – (1) a background signal is established where HONO is photolyzed but the 308-nm laser is tuned off-resonance (S_1), (2) both ambient OH and the OH fragment from HONO are excited by tuning the 308 nm laser to on resonance (S_2), (3) the 355-nm photolysis laser is blocked by a shutter and background signal is re-established by tuning the 308-nm laser off-resonance (S_3), and (4) the 355-nm laser is still blocked but ambient OH is excited by tuning the 308-nm laser on-resonance (S_4).

L211/L213: There is inconsistency in the naming of the quantum yield.

This typo has been corrected.

L233/234: The term "effective sensitivity" is rather confusing in this context. The sensitivity of the instrument does not depend on laser power due to the normalization of the fluorescence signal to the laser power. The authors likely mean a better limit of detection that can be achieved at higher laser power, because the total fluorescence counts increase and is therefore more likely larger than the noise. Please clarify.

We have replaced the term "effective sensitivity" with "limit of detection" on page 7 of the revised manuscript as suggested.

L233/234: The authors argue that photolytic interferences become smaller in the single-pass configuration compared to the multi-pass configuration. This would allow to operate the system at higher laser power. This is rather confusing because at higher laser power photolytic interferences will again gain in importance. Please clarify.

While the single pass design does not eliminate potential laser generated interferences, we have clarified that the single pass design significantly reduces laser-generated interferences compared to that produced by the multi-pass design at the same laser power. This has been clarified on page 7 of the revised manuscript.

However, while the single pass design does not eliminate potential laser-generated interferences, it significantly reduces laser-generated OH from reactions R4 and R5 as there is no beam overlap and the smaller beam size reduces the potential for double pulsing of the sampled air compared to the multi-pass design at the same laser power. This allows for higher laser powers to be employed in the single pass instrument, improving the limit of detection with significantly lower laser-generated interferences.

L242: What do the authors mean with "once a stable concentration OH and HO2 is produced"? What does need to stabilize?

The concentration of OH and HO$_2$ depend on both the lamp flux and water vapor concentration, which take some time to stabilize at the start of the calibration. This has been clarified on page 7 of the revised manuscript.

Once a stable concentration of OH and HO$_2$ is produced in the calibrator after the lamp flux and water vapor concentration have stabilized, the photofragmentation efficiency (PE) of HONO is determined by adding an excess of NO (approximately 800 ppb) to the calibrator to convert the known concentrations of OH and HO2 into HONO through the HO$_2$ + NO → OH + NO$_2$ and OH + NO → HONO reactions.

L249: How was the loss of 5% determined?

The 5% loss was determined by model simulations of the chemistry. This has been clarified on page 7 of the revised manuscript as described below in response to the following comment.

L250: It would be beneficial for the reader to know the wall loss rates that are assumed and to specify the fractional loss to specific loss processes.

The loss of radicals in the calibrator in the absence of NO was measured as described previously by changing the location of the light source in the calibrator (Dusanter et al., 2008). The measured decrease in the concentration of OH as a function of distance from the exit of the calibrator was found to be approximately 20-30% for a reaction time of 80 ms and a flow rate of 10 slpm. In the absence of added NO this loss rate is due to both loss on walls of the calibrator as well as loss due to radical-radical reactions such as the OH + HO$_2$ reaction. Model simulations were then conducted to determine the relative contribution of radical-radical reactions and wall loss to the overall loss of radicals in the calibrator. From these simulations, a first order loss rate of 2.6 s^{-1} is needed to match the observed loss of OH radicals in the calibrator in the absence of NO. When 800 ppb of NO is added to the calibrator, model simulations suggest that wall loss in the calibrator contributes to less than 3% of the total loss of OH radicals, with the OH + HO$_2$ reaction contributing to less than 2%, as the OH + NO reaction contributes to greater than 95% of the total loss of OH radicals. This has been clarified on pages 7-8 of the revised manuscript, and we have included examples of these simulations as a new Figure 5 in the revised manuscript.

Figure 5 illustrates model simulations of the conversion of OH and HO_2 into HONO using the RACM2 mechanism constrained to the concentrations of water vapor and oxygen. After production of OH and HO_2 in the illuminated region of the calibrator (first 10 ms), reactions with NO lead to the production of HONO after the approximate 80 ms residence time inside the calibrator. In these simulations, the photolysis of water vapor is adjusted to produce approximately 1 ppb of both OH and HO_2 in the calibrator, which in the absence of NO decreases after illumination due to loss from radical-radical reactions and surface loss (Fig. 5). During typical OH sensitivity calibrations, measurements of the loss of radicals in the absence of NO is measured by changing the location of the light source relative to the exit of the calibrator (Dusanter et al., 2008). These measurements indicate that 20-30% of the OH and HO_2 radicals produced are lost due to reaction with the calibrator surfaces as well as loss due to the OH + HO_2 reaction. Model simulations indicate that a first order loss rate of 2.6 s^{-1} is needed to match this observed loss of OH radicals in the calibrator in the absence of NO, and this loss rate has been included in the simulations (Fig. 5). However, these simulations suggest that during photolysis efficiency calibrations, the excess of NO is sufficient to ensure that reaction with NO is the dominant radical sink accounting for greater than 95% of the total loss of OH, with less than 3% of the OH radicals lost via surface reactions and less than 2% lost by the OH + HO_2 and other radical-radical reactions.

L252: The text sounds as if there is a significant fraction of OH left, but Fig S4 suggests that this is negligible.

We have revised this text as suggested on page 8 of the revised manuscript.

Model simulations of this chemistry also suggest that after addition of NO, the OH and HO_2 concentrations are negligible and the concentration of HONO is nearly equal to the total OH and HO_2 concentrations produced by the calibrator (Fig. 5).

L252: Can the authors exclude that reactions of NO from the calibration source leads to any back-reaction of OH to HONO after the 355nm laser pulse has been applied in the measurement cell?

Model simulations indicate that reformation of HONO from reaction of the OH fragment with the added NO is negligible due to the reduced concentrations of both OH and NO in the low-pressure detection cell and the short reaction time between the photofragmentation and excitation laser pulses. This has been clarified on page 8 of the revised manuscript.

Model simulations indicate that reformation of HONO from reaction of the OH fragment with the added NO is negligible due to the reduced concentrations of both OH and NO in the low-pressure detection cell and the short reaction time between the photofragmentation and excitation laser pulses.

Figure 4/5: Are really counts shown or normalized count rates? Why are numbers in Fig. 4 so much smaller compared to numbers in Fig. 5, if they are also derived from calibration measurements?

Both figures illustrate the measured count rates and are not normalized for differences in the excitation laser power or the initial radical concentration between the two different calibration experiments, which accounts for the factor of 2 difference in the measured counts illustrated in these figures. This has been clarified in the caption of Figure 4.

Figure 4: Sample measurement cycle from the LP/LIF instrument during measurement of OH and HONO during laboratory calibrations. The raw signal has not been normalized for the power of the excitation laser or the total radical concentration produced by the calibrator. S_{bkg} is the average of the offline signals S_1 and S_3

L267: It is not very clear for the reader, which correction is applied to S_OH. Is this needed because different losses apply, if NO is added or not? Number of corrections may help to better understand what is done.

This is the correction to account for the 20-30% loss of radicals in the absence of NO due to both radical-radical reactions and radical loss of the walls of the calibrator measured as described above. This has been clarified on page 8 of the revised manuscript.

This can also be written as the ratio of net HONO signal to the initial OH signal, after corrections to account for the 20-30% OH radical loss due to the OH + HO$_2$ reaction and reaction on the walls of the calibrator based on measurements in the absence or NO as described above ($S_{initial\ OH,corr}$).

L271: The authors mention several possible problems with impurities of the NO added in the calibration procedure. This discussion should be extended by a quantitative estimate, if these reactions could play a role for the conditions described in this work.

We have included model simulations to illustrate the potential impact of NO2 impurities in the added NO on page 8 of the revised manuscript, as suggested.

Impurities in the added NO that react quickly with OH and compete with reaction of NO, such as NO$_2$, could lead to apparent lower photofragmentation efficiencies by reducing the amount of HONO produced in the calibrator. Model simulations suggest that a 5% NO$_2$ impurity could reduce the production of HONO by approximately 10% due to reaction of OH with NO$_2$ instead of NO (Fig, 5). As a result, the NO added should be of high purity, and chemical scrubbers designed to reduce impurities such as NO$_2$ should be used.

L282: It would help to give a quantitative estimate about the impact of a typical additional OH concentration during midday on the limit of detection of HONO.

Using the maximum OH sensitivity, laser power, and photofragmentation efficiency described on page 8 of the revised manuscript, a daytime maximum concentration of OH of approximately 4×10^6 cm^{-3} would increase the estimated HONO limit of detection by approximately 20%. This has been clarified on page 9 of the revised manuscript.

For the highest sensitivity, 308 nm laser power and photofragmentation efficiency described above, a daytime maximum concentration of OH of 4×10^6 cm^{-3} would increase the HONO limit of detection by approximately 20% (10 min average).

L283: Typical accuracies for the determination of OH concentration in a calibration source like used in this work are within the range of 10 to 20% and would significantly contribute to the overall uncertainty of the HONO calibration. Please clarify.

The estimated uncertainty of 35% for the HONO measurement includes the uncertainty associated with the OH measurement (18%). This has been clarified on page 9 of the revised manuscript.

The overall calibration uncertainty is estimated to be 35% (1σ), including the uncertainty associated with the OH calibration (18%, 1σ), and depends on the precision of the photofragmentation efficiency measurement.