

RC2: Reply to anonymous Reviewer #1 (15 Dec 2021)

Dixneuf et al., present an inter-comparison of nitrous acid by open path IBBCEAS and LOPAP instrument in SAPHIR chamber in 2011. They show a good performance of this cavity enhanced absorption technique in measuring HONO, they also compared the measured NO₂ and MACR with CLS and PTR. This paper is well written and I only have the follow comments need to be addressed.

Reply: We would like to thank the reviewer for the interesting comments which we addressed as good as possible and reasonable.

RC2:

1. The measurement of MACR by IBBCEAS should also be mentioned in Abstract.

Reply: The detection of MACR was already mentioned in the abstract. We included the estimated 2 sigma detection limit. The following sentence:

“Methacrolein was also detected at mixing ratios below 5 ppbv.”

was changed into

“Methacrolein (MACR) was also detected at mixing ratios below 5 ppbv with an estimated 2σ detection limit of 340 pptv for the same integration time.”

RC2:

2. With respect to the sensitivity change of IBBCEAS in 11 July, is it possibly caused by the unknown vibration and changed the coupled optical system, that means the effective reflectivity may be decreased largely, maybe you can use the retrieved O₄ as a tracer to make it clear. If the Reflectivity changed, the intensity of the spectrum before and after the time point of 09:15 maybe also have a large difference.

Reply: We think that the change in noise in the HONO retrieval after 9:15 hrs on July 11 is not caused by a sudden change in the mirror reflectivity. No relative reflectivity changes were detected on the day (see also comment 4 below); furthermore the change in noise should in case of optical misalignments also be observed in the retrieval for NO₂ and MACR after 9:15 hrs, which does not seem to be the case.

Moreover, O₄ cannot be used as tracer in an open path setup. In IBBCEAS the transmission spectrum without the target species, $I_0(\lambda)$, must be known before the transmission with the target species, $I(\lambda)$, is measured; see eq.(1) in the manuscript. In an open path setup, like in the present case (with e.g. target species HONO, NO₂ and MACR), the spectrum $I_0(\lambda)$ is taken in a clean and dry air-filled chamber. The spectrum I_0 thus already contains the information on the known O₄ absorption bands at 360 and 380 nm, i.e. the bands that are relevant here. Since the spectrum $I(\lambda)$ also contains the same bands due to the O₄ concentration remaining constant in good approximation, (provided substantial temperature variations that may impinge on the equilibrium concentration of O₄ can be neglected.

Therefore O₄ cannot be used as a tracer for the reflectivity. That is also reason why O₄ was not need (nor incorporated) in the retrieval of HONO and NO₂ mixing ratios.

RC2:

3. Line 285 please provide more details of the calculation of effective reflectivity in the text to make this section easier to follow.

Reply: We are not quite sure what else to say here in the manuscript.

$$R_{\text{eff}}(\lambda) = 1 - \left(\frac{I(\lambda)}{I_0(\lambda) - I(\lambda)} d\varepsilon(\lambda) \right) \quad (\text{R1})$$

If the mixing ratio of NO₂ is known from a CLS measurement (in an otherwise clean chamber) then ε is known from the known cross-section spectrum of NO₂. By measuring I_0 and I and knowing the effective cavity length d , the reflectivity spectrum can be calculated. This approach is well known from numerous other publications. We included the review (Ruth et al. 2014) to guide the reader to secondary literature concerning this aspect.

RC2:

4. The open path IBBCEAS can calibrate alone by an anti-reflection coated optics, why the authors calibrated again by the CLS NOx and then compared with the result of CLS NOx?

Reply: Once the reflectivity, R_{eff} , is known from an NO₂ calibration measurement, the optical loss of the low loss (anti-reflection coated) optic (LLO) can also be measured accurately. This is typically done at the time of the initial calibration of R_{eff} . The low loss optic can then be used to determine the reflectivity, using the latest “up-to-date” I_0 measurement, typically taken in the morning after extensive overnight flushing, when the chamber is clean. However, during an experiment with sample mixture in the chamber, the LLO is merely used to check for changes in the reflectivity. In the clean chamber in principle the LLO essentially takes the place of the NO₂ calibration gas. In the filled chamber, however, insertion of the LLO cannot be used to independently measure absolute reflectivities anymore but only relative changes of same. With target species (and additional loss) in the chamber, one can only retrieve the absolute reflectivity, if I_0 has not changed since its last measurement (in the morning for example). Hence one cannot distinguish between a change of R_{eff} and a change of I_0 based on the LLO measurement (compare eq. (2) in the manuscript). One can however figure out how far the setup has drifted from the initial measurement (typically in the morning).

This again is a problem of open path measurements where I_0 cannot easily be established at regular intervals. In closed path setups (extractive instruments) an accurately calibrated LLO can be used for reflectivity calibration because a new I_0 spectrum can be created easily enough every time the reflectivity is to be checked based on eq. (2).

It is recommended to check from time to time how accurate the calibration of the LLO still is. In the manuscript we showed typical calibration measurements in the supplementary material using NO₂ (Figure S5) and the LLO (Figure S6).

We left the text in the manuscript.

RC2:

5. How about the stability of Reflectivity day by day?

Reply: I_0 was taken in a clean and dry chamber every morning and the reflectivity was measured accordingly. R_{eff} calibrations using the calibrated low loss optic were taken at around the same time, in the clean and dry chamber. Over the course of the day several measurements using the LLO were taken regularly, to check that no drift were occurring. This was done together with regular stray light measurements regularly (changes mainly with roof opening/closing). On the days on this paper no dramatic changes beyond the errors stated in the publications were observed (compare Figure S5).

RC2:

6. Line 326, “see Table in the AMT...” please rewrite it with more professional form and cite the Reference.

Reply: We changed the phrase to
“- see Table 1 in the publication by Jordan and Osthoff, Atmos. Meas. Tech., 13, 273-285,
2020 (doi: [10.5194/amt-13-273-2020](https://doi.org/10.5194/amt-13-273-2020)).” We also included some extra information concerning
this comparison in the supplementary material.