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Atmospheric
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Discussions

Interactive comment on “Implementation of an IBBCEAS technique in an atmospheric simulation chamber for *in situ* NO_3 monitoring: characterization and validation for kinetic studies” *by* Axel Fouqueau et al.

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First of all, the authors would like to thank the anonymous referee for this discussion and its constructive comments, corrections and suggestions that ensued. We have carefully replied to all its comments and the paper has been improved following its recommendations. All technical corrections suggested by the referee have been carefully performed. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the comments:

1. There are multiple missing references to figures and tables: L.104, L.150, L.171, L.196, L.213, L.227, L.247, L.295, L.336, L.349, L.356

The authors thank the anonymous referee for having pointed out these mistakes, which are probably due to an error during the submission process. All the references have been added as suggested (L.104, L.152, L.173, L.202, L.220, L. 234, L.257, L.311, L. 367, L.380, L.387).

2. Further technical details should be supplied about L.116: LED optical power

It was indeed not clearly given, but the letter K in the description of the LED indicates the bin of radiant flux (K being between 390 and 430 mW). We modified the text as follows to add this information: P.2.2 L.117: “max. 430 mW”.

L.146: specific RH range of the experiments

Information on relative humidity has been provided P2.2 L.148: “(RH < 1 %)” and P.4 L.289: “The chamber was first filled with dry synthetic air (RH < 1%)”.

L.280-90: To form NO3, either O3 is needed with NO2 to form NO3, or N2O5 must be added as a precursor. This information is missing in the description. The authors should supply these experimental details along with relevant chemical equations.

As suggested by the referee, NO3 generation protocol is now explained in the manuscript (The following text has been added between P.4 L.293 and L.298): “NO3 radicals were then formed in situ, using thermal dissociation of N2O5 (R. (1)), which was synthesized in a vacuum line following the reaction between O3 and NO2 (R. (2) and R. (3)). This protocol was adapted from (Atkinson et al., 1984; Schott and Davidson, 1958) and is detailed in Picquet-Varrault et al., 2009.(reactions)“

L.270: The NO3 concentration should be stated explicitly. Presumably the concentration was zero? How would other absorbing species like NO2 influence the fit variability?

It was probably not clear enough in the manuscript, but this value was estimated by considering the noise of a time profile of NO3 concentration. The concentration was thus not zero. A precision has been added in the text (P.3.4 L.279): “NO3 concentration time profile”. To answer the second question, it should be said that, in this wavelength range, spectral signatures of NO2 and NO3 are very different. Furthermore, NO2 is well constrained by several thin absorption bands. The fit program handles the subtraction of NO2 very well and the fit of NO3 is thus not strongly impacted by its absorption. The fit variability due to NO2 influence has been verified by constraining on the same spectrum different values of NO2 concentration ($\pm$ 100 ppb of the real value). The uncertainty on NO2 fit can lead to an uncertainty of max. 5 ppt on NO3 fit. This value appears to be very satisfying, considering that an error of 100 ppb on NO2 concentrations is very unlikely.

3. It is not clear how the authors calculated certain values. These figures need to be checked: L.177: I calculate 3.15 km for R = 0.99974 and d = 0.82 m, whereas the authors report 3.4 km. Also, it should also be clarified that this is the pathlength across the full optical cavity length (82 cm) and includes the purge volumes. When purging, the effective pathlength would be about 25% shorter.

The effective path length was calculated using Eq. 4. The value of 3.4 km is indeed an error, and it has been corrected in the manuscript (P.3.4 L.185).

This value was calculated for a full optical cavity length (82 cm) and does not include the purge volumes. A sentence has been added to specify that the purge was not used during this study (P.2.2 L.111): “Nitrogen flush was not used in this study, but is available for further type of experiments.” The effective pathlength when purging is indicated in P.2.2 L.110.

L.182: I calculate 12% variation, not 20%

It was a mistake and it has been corrected in the manuscript (P.3.1 L.183).

4. The authors should comment briefly on photolysis of NO3 by the IBBCEAS probe

beam, potential surface losses of reactants, and the influence of water vapor and aerosols on the spectral analysis. These issues are likely unimportant for kinetic experiments, but should be noted for completeness.

In the used wavelength range, only one photolysis reaction can occur: for λ < 710 nm, NO3 is dissociated into NO and O2. Nevertheless, it has been shown that for λ > 640 nm, quantum yield of photolysis is close to 0, and thus suspected close to 0 at 662 nm. But even though NO3 was slightly subject to photolysis locally, the volume enlightened by the probe beam is very small in comparison to the overall volume of the chamber (< 0.04%). The homogenization system allowed a mixing with the rest of the volume. Finally, the intercomparison experiment shows that this eventual loss is not significant because it would have led to lower concentrations measured by the IBBCEAS than the FTIR. So the kinetic method is not impacted by a loss of NO3 due to photolysis. A precision has been added P.4 L.330: “Finally, the intercomparison experiment shows that an eventual loss due to photolysis of NO3 by the beam is not significant because it would have led to lower concentrations measured by the IBBCEAS than by the FTIR. In addition, for wavelength longer than 640 nm, which is the case here, Johnston et al., 1996 have shown that photolysis quantum yield is close to 0. It is thus expected that the photolysis of NO3 in the used wavelength range is not occuring. Furthermore even though NO3 was slightly subject to photolysis locally, the volume enlightened by the probe beam is very small in comparison to the overall volume of the chamber (< 0.04%) and the homogenization system allowed a mixing with the rest of the volume.” The authors expect that wall losses of NO3 are occurring. Nevertheless, as mentioned by the referee, the absolute kinetic method consists of measuring the decay of trans-2-butene and to use the NO3 concentration measured during the decay. Then, NO3 additional losses do not affect the rate constant determination. A sentence was added in the manuscript in order to precise this point (P.5 L.360): “It is important to notice that the absolute kinetic method used consists of measuring the decay of trans-2-butene for a known concentration of NO3, and not the decay of NO3 radicals for a known concentration of the VOC. The method is thus not affected by NO3 additional loss processes (e.g. wall losses, reactions with NO2 or with peroxy radicals). Only additional losses of the VOC would lead to an overestimation of the rate constant. This was checked prior to the experiments (i.e. before in the injection of N2O5) and no significant loss of the VOC was observed in the timescale of the experiment (see below)." There is a very strong water vapor absorption in the wavelength range used. Nevertheless, all experiments have been performed in dry conditions and no water features were present on the spectra. A sentence has been had P.2.2 L.147:"Absorption by water vapor may be very high under atmospheric conditions." Aerosols can also affect the IBBCEAS technique at two levels: i) in general, deposition of aerosols on the mirrors lead to a decrease of their reflectivity. That has been dealt with the nitrogen purge in case of the generation of aerosols. ii) The absorption and scattering of the beam by aerosols can lead to a major decrease of the signal in the used wavelength range. In this study, no SOA was formed in the chamber, causing no such problem. In case of the use of the technique with a system which produces SOA, experimental conditions have been modified by using the nitrogen purge close to the mirrors surface and by reducing the production of SOA (by reducing the concentration of precursor).

5. It is not entirely clear how the effect of I0 stability has been determined. Is the 3% change in NO2 concentration seen at all concentrations, or is it a typical or worst case scenario? Can losses to walls influence the analysis? The residual in Fig. 3 looks very much like the NO2 absorption spectrum, so why does fitting with the NO2 cross-section not eliminate these features better?

The impact of I0 stability has been evaluated by performing 2 types of experiments: First, the stability of the optical system has been verified. For this purpose, long term measurements of the signal have been done, leading to intensity variations lower than 0.3% and to very small baseline distortions. Then, the impact of these baseline distortions on the quantification of the absorbing species has been evaluated by measuring the evolution in time of the concentration of a stable species, here NO2. A mixture of 1 ppm of NO2 in synthetic air was used. A sentence has been added in the manuscript

(P.3.2 L.193): "two types of experiments have been performed: first, the stability of the optical system has been verified. For this purpose, long term measurements of the signal have been performed, leading to variations lower than 0.3% and to very small baseline variations. Second, to verify the impact of these variations on quantification of the absorbing species, experiments were conducted [. . .] Then, a concentration of NO2 was introduced into the chamber (mixing ratios ranging between 100 ppb and 1 ppm, depending of the experiment) and the signal I(ïĄň) was measured" and P.3.2 L.202: "for a concentration of 1 ppm of NO2." It looks very unlikely that wall loss can influence the analysis, because the concentration is measured and decay would have been observed and NO2 is very stable in the CSA chamber. In addition, NO2 concentration is not constrained for the fit so in the case NO2 concentration was not stable, the fitted concentration would be lower. The referee is right when saying that the residual looks like NO2 absorption spectra. It can be explained by a deformation of the baseline in time, due to the remoteness of I0, which prevents the software to fit correctly the NO2 spectra. It is likely that the residual is composed of both this baseline deformation and the small part of NO2 cross section that is not correctly subtracted. The uncertainty generated by this phenomenon is said in the manuscript P.3.2 L.202 (up to 3 % for NO2 concentration measurements).

6. For the detection limit calculation, the authors should specify whether this calculation is for a purged or unpurged system.

The detection limit was calculated without the purge system. It has been specified P.3.3 L.214 in the manuscript: "and an unpurged system,"

7. The calculation of the detection limit is based on the signal-to-noise ratio for a single wavelength. However, the spectral fit is constrained by many independent signal measurements at different wavelengths. The authors should evaluate how the multiplex nature of the measurement affects the system's detection limit.

We indeed used the classical method to determine the detection limit: it has been calculated on the signal-to-noise ratio for a range of wavelength between 655 nm and 666 nm, and we used the max. value of NO3 absorption. This spectral range presents high absorption of NO3 and weak absorption of NO2, as said in the answer to the question 2, L.270. It should be said that in real conditions, as shown in figure 4 in the manuscript, 6 ppt of NO3 are very close to the detection limit. The determination of the detection limit is thus coherent. Furthermore, this figure shows a spectrum with 630 ppb of NO2, which is an important concentration. The detection limit is not degraded by the absorption of NO2.

8. Figure 6: At low pptv, it looks like there's still an IBBCEAS signal for NO3 but no FTIR signal. Does this divergence reflect a difference in instrument sensitivities, or equilibrium/heterogeneous chemistry, or some other cause? Please comment.

By looking at the data, it seems that this case is for the first two points ([NO3]FTIR = 3.0 ppt; [NO3]IBBCEAS = 6.5 ppt and [NO3]FTIR = 4.6 ppt; [NO3]IBBCEAS = 6.7 ppt). For higher concentrations, the agreement is very good. It seems reasonable to think that the sensitivity of the FTIR measurement can explain this difference: it is based on the measurement of NO2 and N2O5. At this moment, N2O5 concentrations are small (approx. 8 ppb) which is close to the detection limit of the FTIR for this species (approx. 6 ppb). The uncertainty of this measurement is thus high, which can explain this difference at very small concentration of NO3. Please note also that these concentrations are close to the detection limit of the IBBCEAS, so it will not be used in the frame of a kinetic experiment.

9. L.313: Are spatial inhomogeneities in gas concentrations expected in the chamber?

During experiments, a homogenization system is used to prevent from inhomogeneities of the mixtures. It is constituted in three parts: (i) an injection pipe, allowing injecting all along the chamber, ii) two fans, allowing a homogenization of gas inside the chamber and iii) a close-circuit homogenization pump, which samples in one extremity to inject the mixing back in the other one. Experiments have been conducted with an

inert gas (NO2) in order to measure the mixing time. Measurements were done in several points of the chamber. This system thus allows a mixing time inferior to a minute. The good agreement between the two measurement methods in the intercomparison experiment, which measure in two different areas, shows also that there are no major inhomogeneities. A sentence has been had to explain it better in the manuscript P.2.1 L.61: “It is equipped with a homogenization system which is made of i) an injection pipe (4 meters long, 1 cm diameter and regularly drilled with 1 mm holes) which allows to inject the reactants all along the chamber, ii) 2 stainless steel fans allowing a homogenization of gas inside the chamber and iii) a close-circuit Teflon pump connected at both ends allowing a recirculation of the gas mixing. This system allows a mixing time below one minute.”

10. Figure 7. NO3 and butene losses are very rapid. Would data quality be increased by selecting reaction conditions to produce a slower reaction and more data points?

For the kinetic of trans-2-butene, it was not necessary to increase the frequency of the measurement because the rate constant is relatively low. For faster kinetics, experimental conditions can be changed, in particular by reducing VOC concentration or increasing the measurement frequency.

11. Most of the uncertainty in the kinetic data arises from the uncertainty in the FTIR results. Calibrated CIMS or PTR-MS might be better suited for co-measurement of VOCs. The authors may want to discuss these considerations for their kinetic studies.

We fully agree with the referee that PTR-MS measurements might have been more precise. Unfortunately, this instrument was not available in our group when we performed the experiments.

Minor corrections:

L.27: either “the NO3 radical has. . .” or “NO3 has. . .”

It has been done.

L.38: “one of the reasons for this. . .”

It has been done.

L.46: “progress has been made”

It has been done.

L.53: “For this purpose,”

It has been done.

L.63: “presented in detail”

It has been done.

L.76: “NO_3 was”

It has been done.

L.101: “planar/concave”

It has been done.

L.106: “prevent adsorption of. . .”

It has been done.

L.115: Caption Caption should note that collimating lenses and curved mirrors are not shown on the beam injection side.

It has been done.

L.127: “LED current is fixed at 900 mA”

It has been done.

L.132: “to focus the beam”

It has been done.

L.143: hyphen in reference

It has been done.

L.175: "justifies...wide scale". It is unclear what is meant by this. That it should be measured over a wide wavelength range, or that it is not necessary to do so?

The sentence has been changed to: “which justifies that it is necessary to measure it on a wide wavelengths range”.

L.182: “prior to each experiment”

It has been done.

L.196: “up to 3 % in NO_2 concentration”

It has been done.

Figure 3. Change “residue” to “residual” in figure titles and legends.

It has been done.

L.280: “was first filled with dry synthetic air”

It has been done.

L.281: “Air Liquide NO_2,”

N20 (should be read N-20) is actually the name of the cylinder.

L.287: NO_2 and N_2O_5 concentrations

It has been done.

L.300: in IBI and in the spectral treatment

It has been done.

L389: performance

It has been done.

L.396: Clarify “from ppt to ppt range for NO3“

It has been done.

L.400: Monitoring NO3 radicals

It has been done.

L.409: intercomparison

It has been done.

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