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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.

Anonymous Referee #1

Received and published: 21 May 2020

Fouqueau et al., AMTD: Implementation of an IBBCEAS technique in an atmospheric simulation chamber for in situ NO3 monitoring: characterization and validation for kinetic studies

Fourqueau et al. present the development and characterisation of an IBBCEAS system and its application to NO3 kinetic studies of VOCs in an atmospheric simulation chamber. NO3 was one of the earliest atmospheric targets of optical cavities using ringdown and broadband approaches in the visible region of the spectrum. This work is not new in that respect, nor in the application of such instruments to atmospheric simulation

chambers. Nevertheless, their work goes further than others in applying this method to the determination of absolute rate coefficients in chamber-kinetic studies of VOC oxidation by NO3. The reported rate coefficient agrees well with other absolute rate coefficients reported in the literature.

While the work is probably eventually publishable, there are omissions and questions about calculations that first need to addressed. There are also quite a large number of grammatical errors or typos that should be corrected.

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

2. Further technical details should be supplied about

L.116: LED optical power

L.146: specific RH range of the experiments

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.

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?

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.

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

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 vapour and aerosols on the spectral analysis. These issues are likely unimportant for kinetic experiments, but should be noted for completeness.

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?

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

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.

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

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?

11. Most of the uncertainty in the kinetics 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.

Minor corrections:

L.27: either "the NO3 radical has..." or "NO3 has..."

L.38: "one of the reasons for this..."

L.46: "progress has been made"

L.53: "For this purpose,"

L.63: "presented in detail"

L.76: "NO3 was"

L.101: "planar/concave"

L.106: "prevent adsorption of..."

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

L.127: "LED current is fixed at 900 mA"

L.132: "to focus the beam"

L.143: hyphen in reference

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?

L.182: "prior to each experiment"

L.196: "up to 3 % in NO2 concentration"

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

L.280: "was first filled with dry synthetic air"

L.281: "Air Liquide NO2,"

L.287: NO2 and N2O5 concentrations

L.300: in IBI and in the spectral treatment

L389: performance

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

L.400: Monitoring NO3 radicals

L.409: intercomparison