

## Review of Preprint:

**Article:** Decker, J., Fertein, É., Bruckhuisen, J., Houzel, N., Kulinski, P., Fang, B., Zhao, W., Hindle, F., Dhont, G., Bocquet, R., Mouret, G., Coeur, C., and Cuisset, A.: MULTICHARME: A modified Chernin-type multi-pass cell designed for IR and THz long-path absorption measurements in the CHARME atmospheric simulation chamber, *Atmos. Meas. Tech. Discuss.* (2021), <https://doi.org/10.5194/amt-2021-399>.

The authors describe first measurements and the spectroscopic characterization of a modified Chernin-type multi-pass cell, which has been designed for wavelengths in the IR and THz region. The multipass cell has been set up as part of the detection equipment of the CHamber for Atmospheric Reactivity and Metrology of the Environment (CHARME) in Dunkirk. The combination of this type of multipass cell and a low-pressure atmospheric chamber is novel, and the data presented inspire confidence in the method.

The cell enables path lengths between 120 and 480 m (540 m) in the IR and between 120 m and 280 m in the THz region. Proof-of-principle measurements have been performed with N<sub>2</sub>O and O<sub>3</sub> whose mixing ratios were established. While the sensitivity of the method for those species is modest, its selectivity is a strength, enabling the potential to study less common (polar) VOCs in the future. While the authors address detection limits, applicability of the detection approach, its selectivity and suitability for kinetic studies based on the time resolution during an O<sub>3</sub> reactivity study, I am missing a general comparison with other methods and a classification of the method among other (spectroscopic) approaches in different wavelength regions.

The authors discuss some advantages and drawbacks of their approach. They also describe experimental difficulties and how they were overcome, however, more attention to detail, e.g. in the establishment of the LOD or in the discussion of systematic errors, would be helpful.

The overall presentation of the work is well structured and clear, however, in several places some confusion may arise due to the wording used. The authors give sufficient credit to related work and with a few exceptions most references appear appropriate.

I recommend acceptance of this manuscript for publication after addressing the observations in this review; I consider the large majority of comments as minor.

## Title

L3. Delete the “full stop” at the end of the title.

## Abstract

L20. Improve the sentence: “Moreover, a THz monitoring at low pressure of the ozone decay in the chamber has been performed.”

L25. “to reach atmospheric trace levels.”

L25/26. Improve the sentence.

## Introduction

L30. large panel -> large variety

L31. apparatus -> apparati

L31. laboratory developed -> custom-designed

L36. quantification yielding to kinetic -> quantification of kinetic

L40. Use a uniform way to denote pathlength throughout the manuscript: either “pathlength” or “path length”

L43. define VOC

L45. The classic reference after “White-cell” would be good

L50. Valence -> Valencia

- L55. Even though specific, I would give also credit the older publication here:  
S. M. Chernin and E. G. Barskaya, Optical multipass matrix systems, Appl. Opt. 30, 51-58 (1991).
- L58. Delete “than” before “100 ppb”. Parts per billion should be stated as “by volume”, i.e. ppbv
- L59. Full stop is in the wrong place.
- L62. ...to control the propagation of more divergent beams over long distances...
- L63. Far-IR -> far-IR; trace gases -> trace gas
- L66. comma in reference
- L67. weak -> small
- L69. comma in reference
- L73. If the results were preliminary, they should not be published here. Delete “preliminary”.

### **Experimental setup and Methodology**

- L81. Comma after briefly.
- L82. made in -> made of
- L85. Depending on power and geometry of the fan system and depending on the nature of the reactive species being studied, the stirring of the gas mixture can lead to an increase of wall losses of the reactive species and not to a homogenization. I think this statement may require a reference concerning a study of the effect of the fans or should be phrased more carefully.
- L89. ...filled with purified and dried air at the required pressure using ...
- L91. The Baratron only measure the pressure but do not control it. Is the MKS PR400B connected to a pressure controlling flow meter? If that is the case then that should be pointed out, otherwise there is no component here that actively “controls” the pressure as claimed.
- L94. “...accommodate the MULTICHARME optical ...”
- L96. *et al.* should be not italics. I would cite the original paper here also:  
S.E. Fiedler, A. Hese, A.A. Ruth, "Incoherent broad-band cavity-enhanced absorption spectroscopy", Chem. Phys. Lett. 371, 284-294 (2003).
- L104. so as to anticipate -> to account for
- L106. substrate was -> substrates were
- L110. A supporting reference from a previous Anhui publication would be good here.
- L112. DN 450 access ports (A1 and A2 in Figure S1)... insert a cross-reference to the supplementary material.
- L115. located on opposite ends of the cylindrical chamber.
- Caption Figure 1. ...two mirror's blocks... -> ...two mirror assemblies...  
objective's block -> objective block  
field's block -> field block
- L118. What kind of “static analysis” was performed? Finite element calculation? What conditions (force field) were assumed? Somewhat more detail is required here or an appropriate reference should be stated.
- L127. moving -> movement
- L127/128. Improve sentence: “The five mirrors’ configuration is easy to align, with very good stability to vibrations, and gave variable rows with even column images on the field mirrors.”
- L130. A pathlength of 540 m is claimed here, however, measurements are only shown up to 480 m.
- L132. Extended -> External
- L133. Delete “power” after 80 mW
- L134. Name the photodiode and give some specs. Ge, InGaAs? Bandwidth?  
Name the oscilloscope and give some specs (e.g. vertical resolution, sample rate, max frequency)
- L135. DL source -> laser or -> ECDL
- L142-144. Improve this sentence. To the accuracy of what parameter does the value of  $10^{-7}$  refer to? The wavelength range was calibrated using the Burleigh wavemeter with a specific accuracy? Can you give an absolute value?
- Caption Figure 2: performed -> established; Extended -> External; HRFZ needs to be explained
- L159. Fix the way the reference is cited.
- L162/163. A and  $R_{\text{eff}}$  should be in italics.
- L164. How were the error bars determined? Insert a cross-reference to the caption of Figure 3.

Figure 3. I would plot a power law always in a double logarithmic graph rather than using linear axes. The right axes are missing in panels (a) and (b).

Caption of Figure 3.  $R^n \rightarrow R_{eff}^n$ ; "... , with  $\sigma_i$  being the error bar..."; "... of the controller sensor...". Can the THz power fluctuations also be quantified?

L175. "...using high resolution ..." What are realistic media? What is meant by that?

L179. Can more information be given on the code from LightMachinery Inc.?

L185. Detectors

L189. "...as a function of frequency."

L191. "...He-Ne laser wavelength..."

L198. Delete "important"

L199-201. Rephrase – these sentences are rather casual and should be more factual.

L201. Fix the referencing.

L204. "...exceeded"

## Results and discussion

L214. molecule test -> test molecule

L217. their -> the or its

L218 & 221. Fix referencing (italics)

Figure 4 and L236. The unit on the ordinate of Fig. 4(b) and in Line 236 seems incorrect as far as the axis title is concerned. Depending on what variable the absorption coefficient is integrated over (frequency or wavenumber), the unit should not remain  $[\text{cm}^{-1}]$ , which is the unit of the absorption coefficient itself. What is probably meant here is the "integrated absorbance", then the unit of  $[\text{cm}^{-1}]$  is correct, if integrated over wavenumber.

Caption of Figure 4 & L237 & L238. gaussian -> Gaussian

L236. Is the linear regression going through the origin or was it forced through zero? This is difficult to see in Figure 4(b). With a non-zero intercept the slope may change somewhat. Remedy: State the fit function explicitly.

L238. Unit of slope okay if integration over absorbance.

L240. Kwabia Tchana et al., 2013

L241. "...estimated to be ..."

Based on Figure 4(a) the estimated HWHM seems to be somewhat too small. FWHM seems to be more like  $\sim 0.028 \text{ cm}^{-1}$ .

L241. The equation in that line requires more explanation. How was it derived?

I find  $\alpha_{0,\text{exp}} = s \cdot \sqrt{\ln 2} / (\Delta \nu \cdot \sqrt{\pi})$ , if what was called "integrated absorption coefficient" is indeed "integrated absorbance". If a HWHM of  $0.014 \text{ cm}^{-1}$  is used this results in a similar value as stated, i.e.  $3.92 \times 10^{-6} \text{ cm}^{-1}$ . If the original HWHM is used one finds a value that is even larger, i.e.  $5.50 \times 10^{-6} \text{ cm}^{-1}$ .

What would be of interest here also is to compare this value with the measured  $\alpha_{0,\text{exp}}$ , averaged for all 8 different pathlength measurements.

L254. Where does the integrated line intensity come from? How was this estimated? There is a reference needed here. It also says "experimentally measured". By whom? In this work?

L257. "...to the Doppler one..." -> "... to Doppler broadening..."

L260. I am again a bit confused here as before. How can an integrated absorption coefficient be deduced by integrating over the absorbance (in each case integrated over frequency or wavenumber)?

L265. "...estimated to be ..."

L265. How was  $\alpha_{0,\text{exp}}$  calculated here? A Voigt profile is used for the description of the absorbance of the measured line. What assumption was made?

L268. Give a reference for the line intensity S.

L280: delete "these last years"

L284: "to scattering". Replace "radiations" by "spectroscopy". Change the word "agility"

L285: "rapid" -> "short"

L288: "gas traces" -> "trace gases"

L289: "compared to the optical IR one" -> "are significantly smaller than those of optical IR sources:"

L306: "for four" -> "of four"

L310:  $1.4 \times 10^{-3} \text{ cm}^{-1}$

Figure 6b: Labels on axes are very small

L322: “to” -> “and”

Table 1: Use proper scientific notation in column 3.

L337: “...by fitting..” what? A ‘Voigt profile’? The function that is fitted to the data should be stated here (“...by fitting a Voigt profile...”). Moreover, in Figure 7 the absorbance spectrum of the R(22) of N<sub>2</sub>O line is shown. What do the authors mean by “integrated intensity” in Line 337?

L339: Replace the word “agility” with something meaningful.

L338-342: It should be argued or shown that the “two baseline treatments” have no effect on the line shape and width. A comparison of results with and without the treatment could be shown here, since data manipulations like FFT filtering affect the line shape and hence the error of the resulting number density. A systematic error discussion could be included here.

L343: concentration “N” -> number density

Figure 7: Red and blue circles (or panels) seem to have been mixed up. It would be meaningful to show the fit residuals in panel below the main figures. The unit of the integrated absorbance is stated in MHz, however as per the main text (L344) this should be wavenumbers. Please be uniform in your notation.

L354: What is meant by “... an integrated absorption of 2.4 MHz was fitted ...”? Concentration -> number density.

L354: use scientific notation for the value of the number density.

L356: rephrase “..provides the level of dilution stipulated in the calibrated gas.”

L357: delete “an”

L361: A -> An

L362/363: Rephrase the sentence: According ..., This... analyzer.

L363: “pumped up” -> “pumped down”

L367: Use scientific notation in for the value of the line strength S.

L368: “...from the fit of the line with a Voigt profile ...” -> “...from the fit of a Voigt profile to the line ...”

L375. The pressure should be explicitly state here and not only in the caption of Figure 8. State the chamber conditions better.

L376: “into” -> “in”. “ In this aim” ? 610365.35 (no comma, like in French)

L377: “during” -> “for” Separate the text in L376 – 378 into 2 sentences. Rephrase.

L378: “spectra” -> “spectrum”; “reproduced” is not the right word here -> “repeated”.

L380. “Concentrations” -> “mixing ratios”

L381. “decrease” -> “decreases”

L382. “due mainly due” ? ; “losses” -> “ozone losses” ; “walls chamber” -> “chamber walls”

L382-385. Split the sentence “The concentration decrease was fitted...” into two or three sentences.

What is meant by “...a fit weighted on the estimation of the limit of detection”? This is not clear. The LOD was estimated based on a signal to noise ratio of 1; the authors should say more here. Explain better how the maximal amplitude of the baseline oscillations was determined. Over what spectral region, for what time in the measurement series. What was the maximal signal, S? The integrated absorbance or the max value of the absorbance. In the caption of Fig 8. The authors refer to the “absorbance area”. This is not clear to me.

L386. The LOD should be properly stated; i.e.  $50 \pm ??$  ppmv. ...“we are very close to this limit” is too casual. What is the acquisition time for this LOD, is it 3 min?

Figure 8 caption: Caption should be non-centered. “Fig. 8:” -> “**Figure 8.**” “during” -> “for”. The panels (a) and (b) should not be labelled “Fig.8a” and “Fig. 8b”. Rephrase the sentence “3D plot gathering ...” use different wording. “Weighted on the LODs”?

L395. walls -> wall

L396. “cleaning state”? Cleanliness?

L399. “ozone walls” -> “ozone-to-wall”

L400. “show” -> “showed”

Since the concentrations in the current experiment are significantly higher it is not clear how meaningful this comparison to the work by Itoh *et al.* is. Itoh *et al.* measured from a pressure of 6.7 mbar, which is not even as low as in the present study it seems? The conditions in the present paper

are typical for chamber cleaning activities. Under these conditions it is known that the O<sub>3</sub> loss in the chamber is dominated by wall reactions and not by reactions with O<sub>2</sub>. That is why these conditions are chosen to get rid of impurities, such as volatile organic compounds, on the chamber wall.

L405. “)”)” typo

L406/407. Ozone being generated at atmospheric pressure? I thought the chamber was kept at low pressure in these experiments (see L375.).

L407. “loses” -> “losses”

### **Conclusions**

L415. “...in the THz region”

L417. Measurement at 540 m not shown - no experimental evidence in this paper. The authors may want to include a measurement at 540 rather than just showing an additional long path pattern in the supplementary material.

L426. More consideration should be given to the detection limit(s) in this article; “a few tens of ppmv” is too unspecific.

L433. “such as CHARME”

L436. “middle” -> “medium”

L450. “contributed”

L458. “for its help” -> “for his help”

L463. “JD and JB ...”

### **References**

Many DOIs are missing.

Make the references in the list more uniform.

In the text the citing of references should be uniform. Sometimes et al. is italics, sometimes not, sometimes with comma, sometimes without.

### **Supplement**

The aspect ratio of the photographs in Figure S1 seem non uniform.