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Atmospheric Measurement Techniques Discussions

Interactive comment on "Simultaneous Detection of C_2H_6, CH_4 and δ^{13}C-CH_4 Using Optical Feedback Cavity Enhanced Absorption Spectroscopy in the Mid-Infrared Region: Towards Application for Dissolved Gas Measurements" *by* Loic Lechevallier et al.

Loic Lechevallier et al.

grilli.r@gmail.com

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We thank the reviewer for the very fruitful comments and remarks, which helped us to improve the manuscript. All the remarks from the reviewers have been addressed below, and changes in the manuscript have been done accordingly (highlighted in red).

Reviewer(s)' Comments to Author: Referee #1: This paper deals with simultaneous detection of ethane, methane and carbon isotopic composition of methane by means of

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mid-IR optical feed-back cavity enhanced absorption spectroscopy. The performance of the spectrometer (as obtained in the laboratory environment) in terms of sensitivity and measurement precision makes it suitable for in-situ measurements in ocean waters. In this respect, the scientific motivations are strong and very well highlighted.

The work is performed well and the paper is clearly organized and written, with figures of excellent quality. Therefore, the manuscript deserves publication.

I recommend the authors to consider the comments reported hereafter.

1 (comment from Referee): The spectral region of interest shows a manifold of lines. The authors are obliged to consider 46 absorption lines in the fit of a single spectrum, with a relatively large number of free parameters. To mitigate this issue, physical constraints are applied to some of the parameters, thus reducing the degrees of freedom for the fitting procedure. Since this is one of the key points of the article, more details should be provided. In particular, a careful reader would like to know: the total number of free parameters; the number of experimental points of the interlaced spectrum; the adopted lineshape model.

1 (author's response) : The adapted lineshape model is the speed-dependent Rautian. This information has now be added in the manuscript (page 4) together with the references to the used model. More details about the number of points used for the fit and the degrees of freedom (9 in total) have been added in this section. "In order to reduce the degrees of freedom of the fitting routine and allowing a real-time fit for each acquired spectrum, some of the parameters have been pre-optimized and fixed or linked together. The remaining free parameters are: 1) the spectrum position: the positions of all lines are linked together and only one parameter (which corresponds to the mode-shift) is used to adjust the fit with respect to the acquired spectra; 2) the four intensities of 12CH4, 13CH4, C2H6 and H2O from which concentrations are retrieved, and all lines belonging to one of these molecules are fixed in relative intensity to pre-optimized values, with a single intensity scaling parameter for all of them; 3) the coefficients of

the polynomial function for drawing the baseline of the fit (here corresponding to three parameters for a second order polynomial function); 4) one extra parameter can be added per optical fringes that the operator may want to fit. In this case we only have one optical fringe which has been identified between the output cavity mirror and the signal photodiode. The Gaussian and Lorentzian widths as well as the vVC parameter for Dicke narrowing are optimized line by line and then fixed to their optimum values. The total number of free parameters for the fit is 9 for a spectrum composed by 48 individual points."

2 (comment from Referee): This reviewer has the suspicious that the Voigt model has been used; if this is the case, I recommend the authors to give a look at the paper of Tennyson et al., Recommended isolated-line profile for representing high-resolution spectroscopic transitions (IUPAC Technical Report), Pure and Applied Chemistry, 2014. I am sure that the use of the HTP model would lead to reduced residuals. However, Figure 2 should provide also the residuals for the interlaced spectrum.

2 (author's response) : In the fit routine we used (the Postfit developed by D. Romanini) the HTP model was not developed. However, this should lead to similar results that the speed-dependent Rautian profile used in this work. The difficulty here is more related to the relatively high congestion of absorption lines, which make the fit optimization not trivial. We report the residual of the interlaced spectrum below (in blue) and we adapted figure 2 in the manuscript accordingly. As one can see, the interlaced residual still have some structure related to possible artefacts of the spectra interlacing and some imperfection of the fit optimization. This interlaced spectra is only used for improving the fit parameters which are fixed. During normal operation of the instrument the discrete OFCEAS spectra (black dots) is used.

3 (comment from Referee): Temperature stabilization and control of the V-shaped cavity are requested in order to obtain a high-quality interlaced spectrum. In fact, the authors explain that an increase of the spectral resolution is achieved by slightly scanning the temperature of the cavity (0.02°C of excursion), which causes a shift of the

cavity mode positions with respect to the absorption lines. On page 3, they state that the cavity temperature is stabilized at 308.15 K, giving only two decimal digits. This means that the authors can control the temperature at the level of 10 mK, which is NOT sufïňĄcient for a reïňĄned control of the cavity modes. Nevertheless, reaching the mK level is surely not an easy task. Moreover, the requested equipment would limit the portability of the spectrometer. Such a key point should be discussed.

3 (author's response) : This is indeed a key point that we now better explain in the manuscript. Reaching a temperature stability of the cavity better than 10 mK is challenging. By using a standard PID control and heating bands the temperature stability recorded by a PT1000 temperature probe are below 10 mK (the rms of the red curve in the top panel of Figure 3 is 1.5 mK). However, in this condition, the shift of the cavity mode position with respect to the absorption line positions (mode shift) reaches several tens of MHz. Since the composition of the gas in the cell (and therefore the refractive index) did not change during the measurement, this shift is most probably due to artefacts of the electronic, mainly in the temperature reading but possibly also in the pressure. In order to avoid the shift of the cavity modes, we decided to lock their position with respect to the absorption lines. The position of the absorption lines becomes therefore our reference for maintaining the cavity comb always in the same position with respect to the acquired spectra. This allows a stability of the comb below 1 MHz, while we let the temperature reading fluctuating (by few tens of mK as shown in Figure 3). At page 6 we now added: "The aim of the lock is not to better stabilize the cavity temperature, but to acting on this temperature regulation in order to maintain the cavity comb always at the same position with respect to the position of the absorption lines and compensate for electronic drifts occurring on the circuit for reading pressure and temperature of the cavity." For further clearity we also added at page 4: "This interlacing is only used for fit optimization, while in normal operation the spectra are only composed by data points separated by the cavity FSR (187.4 MHz) with a total of 48 fitted spectral points. " Regarding the temperature measurement, even if we can reach precision of 1.5 mK, on its absolute value we cannot have a better accuracy that 10

mK. That is why we state the temperature with only two digits. The temperature scans of 0.02°C are done in a relatively short time (<1 min), on which long term drifts mentioned above (due to artefacts by the electronic circuit) are negligible. Therefore this relative value of 0.02°C can be stated. In the Labview routine employed for interlacing the spectra is only required to have a linear mode shift evolution oven more than one cavity FSR.

4 (comment from Referee): As for the dependence of the isotopic ratio on the methane concentration, this reviewer would suggest to consider the possibility of a side effect due to the choice of the wrong line shape model.

4 (author's response) : As mentioned above, the speed-dependent Rautian fit was used in this work. We did not try the HTP model as suggested by the reviewer since the model is currently not implemented in the fir routine. Nevertheless, we think that we are limited by the high density of absorption lines in the used spectral region more than by the model used for the fit.

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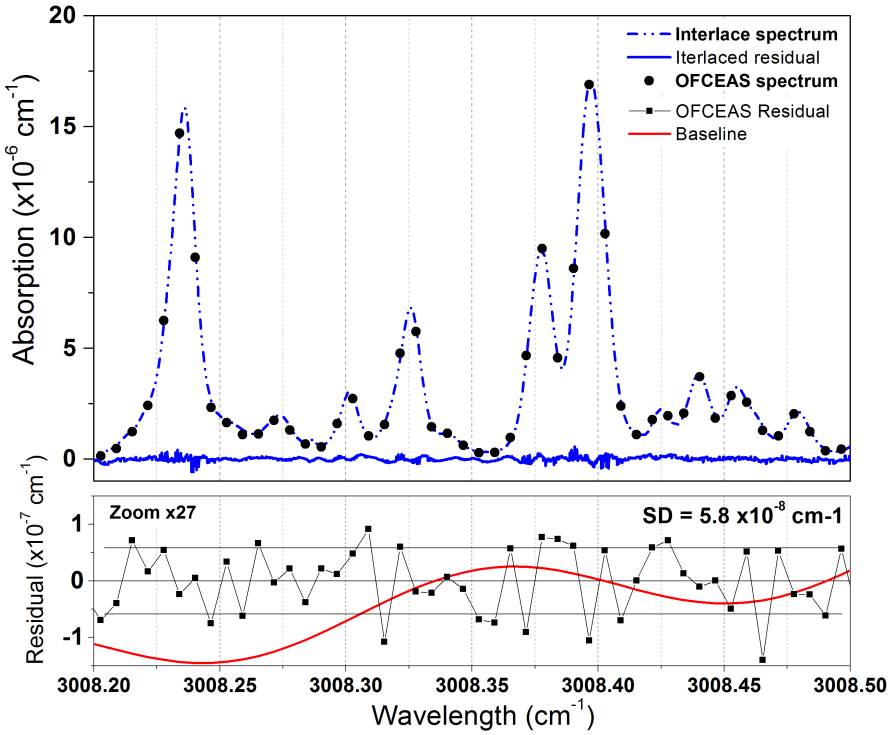

Fig. 1.

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