

-REVIEWER 2

The manuscript is devoted to measurements of the water vapor self-continuum in the two near-infrared spectral regions. Additional experimental data is presented to those already reported by the same group for other spectral regions. The paper is clearly written, easy to read, and present rather important information about water vapor self-continuum absorption in narrow 3-5 mm radius cells in equilibrium conditions. I think this is a good paper to be published in AMT after accounting for the comments described below.

Main issues: 1. The authors often write about the atmospheric application of their continuum measurements. However, all CRDS measurements by Grenoble group have so far been performed in very narrow (3-5 mm radius) cells where conditions for water vapor can be rather different from those in the atmosphere or in much wider FTS cells. I would not raise this issue for many other gases, but water vapor is a specific case. It is interesting that there is rather close agreement between different measurements of the foreign water vapor continuum, but for the self-continuum, the situation is quite different. Different measurements performed applying different methods give very different results up to more than an order of magnitude.

There is some available evidence, including from satellite measurements (see, for example, the Anonymous Referee #1 comment: “The Richard et al. value was considered in developing recent MT_CKD version, but found to not be consistent with the satellite and ground-based observations analyzed in Mlawer et al. (2012)”), to suggest that the water vapor self-continuum absorption in the atmosphere can be much stronger than that obtained from 3–5 mm cells in CRDS measurements. One may suggest that water vapor at low pressures may be, for example, depleted of long-living stable water dimers (with a lifetime ≥ 0.001 s) and/or water nanoclusters in such narrow cells due to their adsorption on cell walls. So, the OFCEAS/CRDS continuum data may be correct for a monomolecular gas, but underestimates atmospheric continuum absorption. I suggest that the authors explicitly recognize this issue in their revision both in their introduction and conclusions.

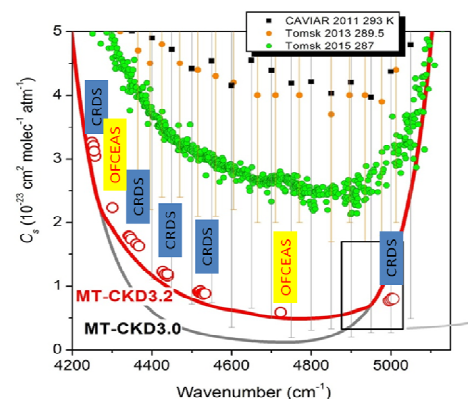
If we summarize, the referee hypothesis is that our laser based setups using narrow diameter cells allow for measuring water continua which are of different nature from those relevant for atmospheric applications, because our water sample are missing some contribution due to “stable water dimers and/or water nanoclusters”. On the other side, FTS measurements with cells of larger diameters are closer to atmospheric conditions and give access to the “real” atmospheric water continuum. In other words, the MT_CKD continuum which is implemented in many atmospheric codes includes a contribution of “stable water dimers and/or water nanoclusters”

Without solid scientific arguments we cannot share this opinion.

Several arguments are in contradiction with this hypothesis on the origin of the discrepancies between CAVIAR and Tomsk measurements (some were already given in Ventrillard et al. 2015).

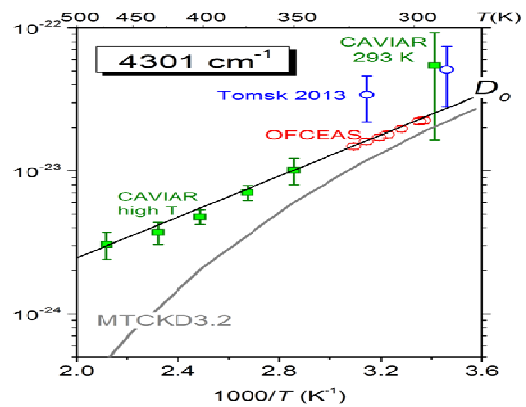
Concerning the influence of the diameter of the cell:

- Our measurements were performed at different periods, by different persons with different setups. Two cavity enhanced techniques were used: CRDS and OFCEAS with cells different by a factor of 2 in diameter (11.5 and 6 mm, respectively). OFCEAS measurements were performed in flow regime while most of the CRDs measurements were performed in static regime. In spite of this variety of experimental conditions we observed a very good consistency of the derived cross section values, for instance in the 2.3 μm window presented below with CRDS and

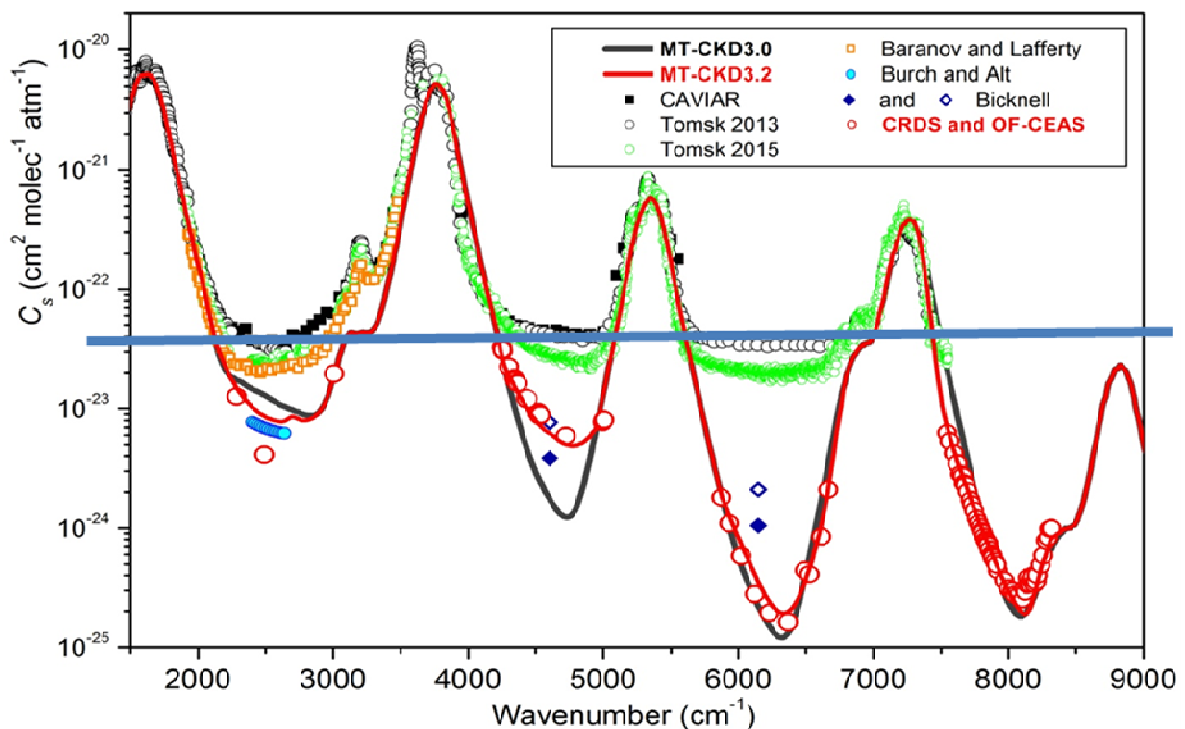


OFCEAS measurements points highlighted. We believe that this indicates that surface effects do not affect our results.

- There is a very good consistency between the FTS CAVIAR measurements at high temperature with our measurements while FTS used large diameter cells and we use small diameter cells. When one considers the following Fig. , it is hard to imagine that the contents of the water sample are different in the FTS high T cell and in the OFCEAS cell.



- The referee opposes our results to all the previous literature results. As summarized by the following figure below, this is not the case. Our results are relatively close to the results by Burch et Alt obtained with a large cell and also by Bicknell et al with air.
- We agree with the reviewer that the CAVIAR and TomsK self continuum high value in the window may be due to droplets or aerosol in the FTS cells. The surface/volume ratio of the cell is higher in the case of CRDS and OFCEAS cells but the quality of the vacuum achieved in long cells with volume as high as 10 m³ cannot be at the level achieved with cells with a 10-100 cm³ volume. For instance, on Fig. 2 of Ptashnik et al., 2013, the TomsK spectra show a “strong contaminating absorption by engine oil at 2800–3000 cm⁻¹”. The TomsK FTS spectra shows also a strong band near 2300 cm⁻¹ due to CO₂ present as an impurity which prevented for continuum retrieval in this region.



According to the referee, the atmospheric water continuum, FTS data (and MT_CKD?) include a contribution of “stable water dimers and/or water nanoclusters” which are destroyed in the CRDS

and OFCEAS cells. If this was the case, we do not see a reason to expect a quadratic pressure dependence of the FTS absorption signal. Otherwise it would mean that this additional absorption due to “water nanoclusters” has also quadratic pressure dependence. Is there some scientific justification of such assumption?

Concerning the Richard et al. value at 2491 cm^{-1} which, according Referee 1 was found to not be consistent with the satellite and ground-based observations analyzed in Mlawer et al. (2012), we were not aware about this fact and have no explanation. OFCEAS measurements of the foreign continuum at the same spectral point may help to clarify the situation.

The fact that our values were used to modify the most recent version of the MT_CKD coefficients indicates that for the developers of the MT_CKD model, our continuum values are relevant for atmospheric applications. Let us underline, that if we compare with the 2.5 version of the MT_CKD model which was the version available prior to our first measurements, the overall agreement of our self continuum in the windows is not bad, in any case much better than with CAVIAR and Tomsk values.

Finally, we would like to insist on the fact that the reliability of all our measurements is supported by the careful checking of the quadratic pressure dependence of the absorption signal. No doubt that critical insights on the discrepancy with CAVIAR and Tomsk will be obtained when similar quadratic pressure dependence will be obtained and published for room temperature continuum measurements by FTS in the windows. Up to now, this is not the case. The reported FTS continua rely on single pressure measurements which leaves open hazardous explanations on the origin of the disagreement, including the presence of clusters or droplets which would not be compatible with a quadratic pressure dependence. (Let us mention that convincing quadratic dependence has been demonstrated by the CAVIAR consortium at high temperature (400 K) in the 0.66-2.0 atm range of water pressure (see Fig. 5 of Ptashnik et al. 2011 and Fig. 9 of Shine et al. 2016)). As mentioned in Shine et al. 2016, the situation is particularly confused considering that “For some of the room-temperature FTS measurements, the whole FTS spectrum was adjusted to assumed values of the continuum strength in either higher or lower wavenumber windows.”

2. Page 9, lines 14-17: “the FTS values are largely overestimated compared to both MT_CKD and the laser measurements. Compared to OFCEAS, CAVIAR and Tomsk 2015 CS values, reported with a 50 % error bar, are overestimated by a factor of three while the FTS values reported by Baranov and Lafferty with a 22% error bar are overestimated by a factor of two”.

This is a somewhat misleading statement. The authors do not take into account the rather strong T-dependence of the self-continuum. They should keep in mind that the OFCEAS data which they show corresponds to about 300 K, while Baranov&Lafferty data are shown for 311 K, and Tomsk-2015 data, for 287 K. To extrapolate to 300 K, the Tomsk data should be decreased by ~30%, while Baranov&Lafferty data should be increased by ~25%.

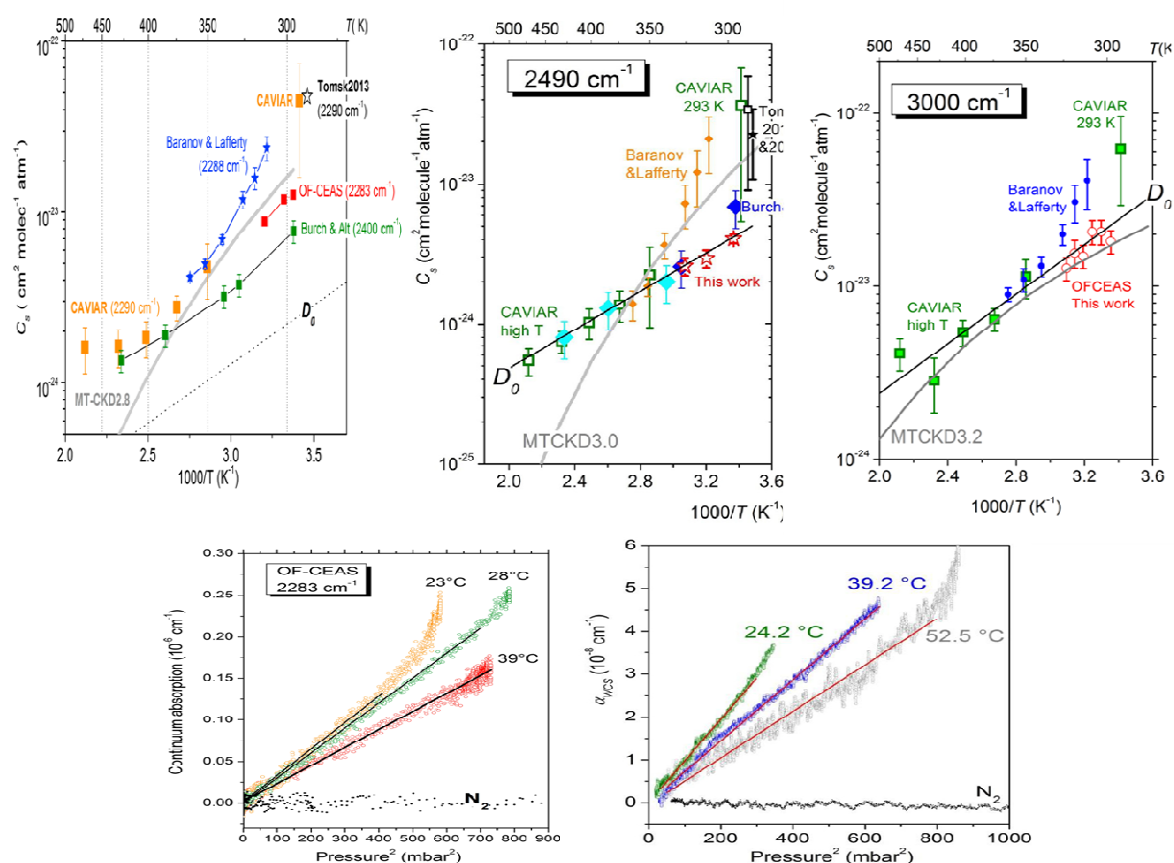
We agree with the reviewer that our comparison did not take into account the fact that measurements were performed at different temperatures. Taking into account the T dependence as proposed by the reviewer, Baranov&Lafferty data (311 K) and Tomsk-2015 (287 K) extrapolated at 300 K are about $C_5 = 5.41$ and $4.53 \times 10^{-23}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$ to be compared to our OFCEAS value at 300 K of $1.96 \times 10^{-23}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$. The text has been modified accordingly:

The CAVIAR C_5 value at 296 K and Tomsk 2015 value at 287 K were reported with a 50 % error bar. A rough extrapolation at 300 K leads to $C_5 = 6.3$ and $4.53 \times 10^{-23}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$, respectively which should be compared to an OFCEAS value of $1.96 \times 10^{-23}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$. The FTS value reported by

Baranov and Lafferty at 311 K with a 22% error bar corresponds to about $5.41 \times 10^{-23} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$ at 300 K.

The T-dependence detected in Baranov & Lafferty's measurements is even stronger than that (see Table 2 in Baranov & Lafferty, JQSRT, 2011 or the left panel of Fig. 7 in the current manuscript). In fact, the Baranov&Lafferty data show a more consistent T-dependence in this window than the present OFCEAS continuum data, and a T dependence which is as consistent, if not more consistent, with independent Baranov & FTS data in this same region. So, I personally am not sure which, of OFCEAS or B&L's data, I should trust in this window. The wording here also needs to be more careful, to make clear that it is specific to near room-temperature.

We agree that the present OFCEAS measurement of the T dependence at 3007 cm^{-1} is not as convincing as that reported at 2283 cm^{-1} in Campargue et al 2016 and at 2491 cm^{-1} in Richard et al 2017. As illustrated by the Fig below, there is nevertheless a good consistency between the OFCEAS T dependence at the three measurement points. The continuum values and T dependence reported by Baranov and Lafferty are systematically larger than ours. And, as mentioned above, our values are supported by the checking of the quadratic P dependence (lower panels of the Fig.).



3. Page 16, lines 5-15: The authors' comments are somewhat misleading in this paragraph, and the authors seem to too easily neglect the results of the FTS measurements. The 0.1–0.2% is a *prediction* of the CRDS measured absorption to the FTS measurement conditions and the argument could be characterized as "circular" – it uses the CRDS measurements to establish that the CRDS measurements must be most reliable!

We have modified the problematic sentence (For instance, in the center of the 4.0 and 2.1 μm windows, at 15 mbar, the continuum signal to be measured leads to a 0.1-0.2 % light attenuation for

an 500 m absorption pathlength) has been changed to (For instance, in the center of the 4.0 and 2.1 μm windows, at 15 mbar, the continuum measured by OFCEAS and CRDS or predicted by the MTCKD model corresponds to a 0.1-0.2 % light attenuation for an 500 m absorption pathlength).

However, the level of continuum absorption measured in FTS experiments in 4 μm window at close-to-room temperatures was not 0.2%, but 1-1.5 % in Tomsk (2013) and 2–3% in Baranov & Lafferty (2011) measurements.

Yes, of course, this is the reason why there is such difference on the C_s values.

These are rather high values and cannot simply be neglected or characterized just as an “error” (Referee #1 comment). Baseline instability was thoroughly investigated both from pure nitrogen and empty cell absorption before and after the sample measurements, and - at least in Baranov & Lafferty measurements - was several times smaller than the measured continuum absorption: “Periodic and multiple tests were made to establish the baseline stability. In recording spectra with the cell filled with pure nitrogen up to about 400 kPa (4 atm), no significant systematic changes in baseline caused by mechanical changes in the cell were observed. With much smaller water-vapor pressures, only a small random scatter within 0.3% (one STDV) was observed. A slow drift of the baseline in time was eliminated by averaging spectra of the empty cell recorded before and after the sample spectrum” /Baranov & Lafferty, JQSRT, 112, 1304-13, 2011/ FTS measurements at different pressures were also performed by Baranov & Lafferty (JQSRT, 2011) in contradiction to the implication at lines 11 to 13 of the manuscript.

For the convenience of the reader we reproduce below the Fig. 4 by Baranov & Lafferty (JQSRT, 2011) to which the reviewer refers:

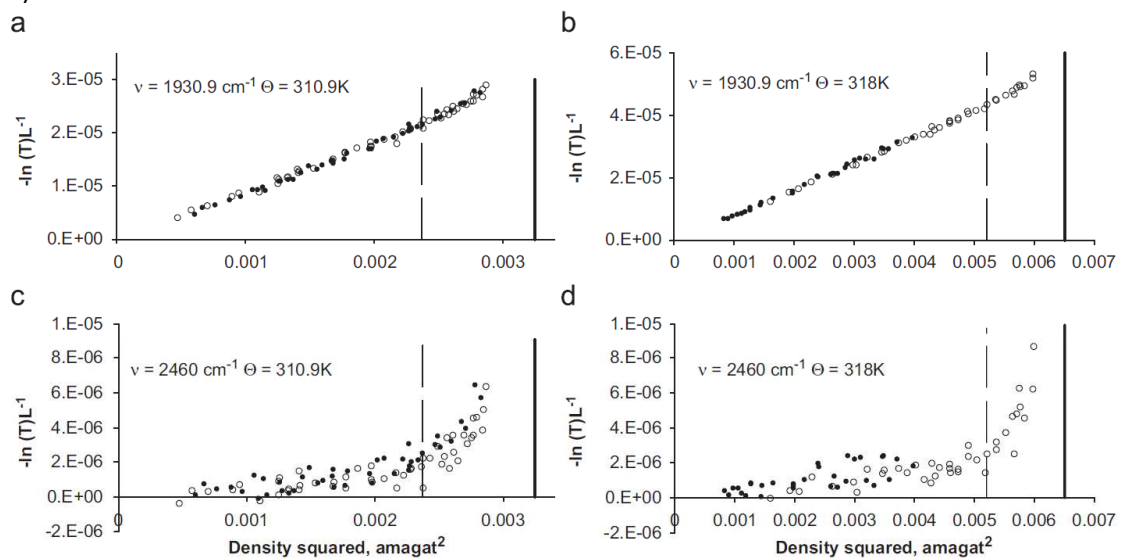


Fig. 4. Measured absorbance in the 1930.9 cm^{-1} micro-window (a, b) and around 2460 cm^{-1} (c, d) at two temperatures. Results observed with an InSb detector are given in circles; dots present measurements with a MCT detector. Solid vertical bars show the water-vapor density limit for a given temperature. Dashed lines give a density cut-off for binary absorption coefficients calculations.

In our opinion, this Figure shows convincing quadratic dependence at 1930 cm^{-1} but not at 2460 cm^{-1} . However, 1930 cm^{-1} is not located in the water transparency window. So to the best of our knowledge, there is no experimental report of the pressure squared dependence of the absorption continuum by FTS in the water transparency windows.

Obviously FTS can be performed at different pressures but the possibility to perform rapid pressure ramps at fixed frequency is an advantage of laser-based techniques and we do not see a reason to modify our text:

The pressure-squared dependence of the absorption signal, systematically fulfilled in the CRDS and OFCEAS studies, provides a crucial test to ensure that baseline variation of the spectra has a gas-phase origin. This is an important advantage of the laser-based approach, to allow monitoring the

pressure dependence of the continuum absorption during pressure ramps lasting no more than a few minutes.

Again in this paragraph a general statement is made about the quality of FTS measurements without specifically clarifying that the argument is only valid at room temperature as is clear from Figure 7 (and there is evidence, discussed above, that the argument may not even valid at room temperature in atmospheric conditions).

We agree that Fig. 7 can be seen as a mutual validation of the high T CAVIAR measurements and our laser-based results. We note that a short path absorption cell was used for the high T CAVIAR recordings and that the measured absorbance were larger as a result of the high water vapor pressure.

Recent FTS measurements in Tomsk, reported at HRMS-2017, 20–25 August, Helsinki, Finland, were performed at several water vapour pressures at 316 K and a path length of 1000 m, and have detected continuum absorption from 4 to 10% with pressure-squared dependence. They agreed well with Baranov & Lafferty's result for 2500 cm⁻¹ window. Therefore, I have serious doubts that self-continuum absorption measured in 3-5 mm radius CRDS or OFCEAS cells can be simply applied to atmospheric conditions before the real reasons for such strong disagreement between CRDS/OFCAS and FTS room-temperature measurements in windows is clarified.

This last point repeats the Main issue (1) – See our answer above.

We are aware about the results presented by the Tomsk group last August in Helsinki for three pressure values between 35 and 56 mbar at 311 K. We could not find the corresponding publication in recent literature and it is then difficult to discuss these unpublished results. Nevertheless, the authors would like to clarify an important point concerning the treatment of Tomsk FTS spectra. According to Shine et al. 2016, in the treatment of their 2013 and 2015 spectra, the Tomsk group adjusted some of their whole FTS spectra to “assumed values of the continuum strength in either higher or lower wavenumber windows”. As indicated in Section 3.2 of Shine et al. 2016, the Tomsk 2013 data rely on the assumption of a negligible continuum value near 9300 cm⁻¹ on the basis of Fulghum and Tilleman's measurements while Tomsk 2015 data rely on a different adjustment: *the absolute level of the measurements was adjusted to be the same as MT_CKD2.5 at 287 K in the 2500 cm⁻¹ window*. We note that since the V2.5 version the MT_CKD model has been importantly modified in the 2500 cm⁻¹ window and then that an adjustment according to the most recent version would lead to important changes on Tomsk2015 data.....

In our opinion, it seems contradictory to claim that the spectra baseline is stable and to perform a global adjustment of the spectra according to assumed value of the continuum. In our experiments, we do not perform such baseline adjustments.

Minor issues:

“Self-continuum” and “Self continuum” – should be unified in the manuscript.

“Self-continuum” is now adopted all along the text.

Page 1, line 18: “completing” is exaggerated. First, the 4 micron window is only covered by 3 measurements and at all wavenumbers the range of temperatures measured, compared to what is needed for accurate atmospheric measurements, is sparse. The authors acknowledge this more correctly at p.17 (10).

Correct. We have changed “completing” to “extending”

Page 8, line 6: “on the order of 30 %.” According to the Table 1, it is rather about 25%”

Corrected

Page 8, line 10: “water continuum represents about 25 % of the measured signal (Fig. 2)”. According to Fig. 2 it is rather 27-30%.

Corrected (28 %)

Figs. 2 & 5: “The contribution of water monomer” is better written as “The simulated contribution of water monomer”.

Done

Page 9, Fig.3: Temperatures should be given for OFCEAS measurements and MT_CKD models. This is particularly important given that the OFCEAS measurements vary significantly over a small temperature interval in Fig. 7, and the degree of agreement with MTCKD at 298 K is not found at all at 303 K.

We have added the temperature information in the caption:

Figure 3: Overview comparison of the self-continuum cross-section of water vapor near room temperature.

Solid lines show different versions of the MT_CKD model at 296 K. Experimental results are obtained using different techniques, namely by OFCEAS, (red circles; Campargue et al., 2016; Richard et al., 2017; this work); by FTS from Baranov and Lafferty (2011), light blue circles, from CAVIAR (black squares; Ptashnik et al., 2011a), from Tomsk2013 (orange circles; Ptashnik et al., 2013), from Tomsk2015 (orange circles; Ptashnik et al., 2015) and with a grating spectrograph by Burch and Alt (1984), dark blue circles. Note that the plotted experimental results correspond to different temperature values (see temperature values given in the insert). The temperature of the OFCEAS results are 296.15, and 297.3 and 298.15 K, for Campargue et al., 2016, Richard et al., 2017 and this work, respectively. The 30-50 % error bars on Tomsk2015 values are not plotted for clarity.

Page 12, line 13: “of the calculated WML contribution calculated as indicated above” – remove the repeated “calculated”.

Corrected. Thank you.

Page 12, line 14: “the WML contribution represents between 18 and 38 % of the total absorption (see Fig. 5)” Again, according to Fig. 5 it is a rather firm 35–38% (nearly independent on pressure). Why do the authors give such uncertain values?

We report measurements at 4 spectral points between 4495 and 5007 cm^{-1} (see Table 1). As indicated in the text, the monomer contribution depends on the spectral point. Here is the table with detailed values for the different spectral points.

WaveNb--	--	Total	Mono	Cs	% Mono/Total
4995.64	--	1.16671E-23	4.14E-24	7.53E-24	35.5
4995.63	--	1.17435E-23	4.14E-24	7.60E-24	35.3
4998.98	--	9.45019E-24	1.79E-24	7.66E-24	18.9
4998.98	--	9.64154E-24	1.79E-24	7.85E-24	18.6
5002.05	--	1.06604E-23	2.74E-24	7.92E-24	25.7
5002.05	--	1.07871E-23	2.74E-24	8.05E-24	25.4
5006.67	--	1.27251E-23	4.80E-24	7.93E-24	37.7
5006.67	--	1.27546E-23	4.80E-24	7.95E-24	37.6

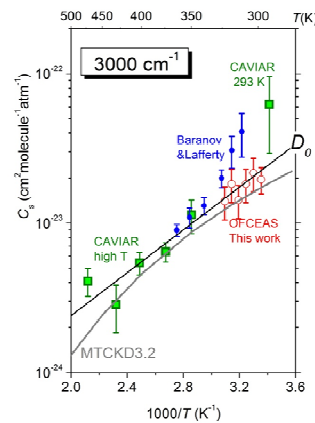
We have slightly modified the text to be even more explicit.

According to the spectral points, the WML contribution represents between 18 and 38 % of the total absorption (38 % at 4995.63 cm^{-1} , as illustrated in Fig. 5).

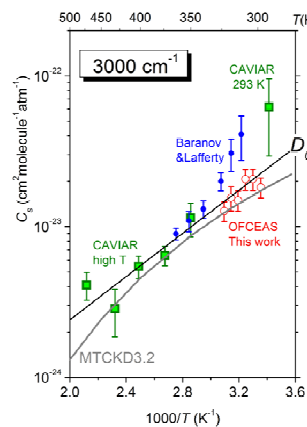
Page 14, Fig 7. The measurements in the 3000 (more properly 3007 cm^{-1}) window do not seem to agree with Table 1. In Table 1, only one point (at 303 K) is over 2.0, and yet 2 points in Fig 7 exceed this value.

We thank the reviewer for this good observation. The previous figure was prepared with preliminary Cs values. It has been updated with the values and error bars listed in Table 1:

New version:



Previous version:



Might the difference between neighboring points also indicate that the authors are too optimistic in their uncertainty estimates?

The (smaller) error bars plotted in the previous version did not correspond to those included in Table 1. We hope that the updated plot showing our claimed error bars will convince the reviewer that our uncertainties are not optimistic.

Page 17, line18: See also 10.1029/2007GL029259 for evidence of water dimers in the region under consideration in this paper.

This reference is now quoted:

Paynter, D. J., Ptashnik, I. V., Shine, K. P., Smith, Pure water vapor continuum measurements between 3100 and 4400 cm^{-1} : Evidence for water dimer absorption in near atmospheric conditions, *Geophys. Res. Lett.*, 34, L12808, doi:10.1029/2007GL029259, 2007.

We thank the two reviewers for their detailed analysis and valuable suggestions to improve the paper. Their interest for the reported work and their detailed discussion are particularly appreciated. We hope that the amended version is now suitable for publication in AMT.