



# Water vapor self-continuum absorption measurements in the 4.0 and 2.1 $\mu\text{m}$ transparency windows



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## ABSTRACT

In a recent contribution [A. Campargue, S. Kassi, D. Mondelain, S. Vasilchenko, D. Romanini, *Accurate laboratory determination of the near infrared water vapor self-continuum: A test of the MT\_CKD model*, J. Geophys. Res. Atmos., 121,13,180–13,203, doi:10.1002/2016JD025531], we reported accurate water vapor absorption continuum measurements by Cavity Ring-down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Absorption Spectroscopy (OF-CEAS) at selected spectral points of 4 near infrared transparency windows. In the present work, the self-continuum cross-sections,  $C_5$ , are determined for two new spectral points. The  $2491\text{ cm}^{-1}$  spectral point in the region of maximum transparency of the  $4.0\text{ }\mu\text{m}$  window was measured by OF-CEAS in the  $23\text{--}52\text{ }^\circ\text{C}$  temperature range. The  $4435\text{ cm}^{-1}$  spectral point of the  $2.1\text{ }\mu\text{m}$  window was measured by CRDS at room temperature. The self-continuum cross-sections were determined from the pressure squared dependence of the continuum absorption. Comparison to the literature shows a reasonable agreement with 1970s and 1980s measurements using a grating spectrograph in the  $4.0\text{ }\mu\text{m}$  window and a very good consistency with our previous laser measurements in the  $2.1\text{ }\mu\text{m}$  window. For both studied spectral points, our values are much smaller than previous room temperature measurements by Fourier Transform Spectroscopy. Significant deviations (up to about a factor 4) are noted compared to the widely used semi empirical MT\_CKD model of the absorption continuum. The measured temperature dependence at  $2491\text{ cm}^{-1}$  is consistent with previous high temperature measurements in the  $4.0\text{ }\mu\text{m}$  window and follows an  $\exp(D_0/kT)$  law,  $D_0$  being the dissociation energy of the water dimer.

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## 1. Introduction

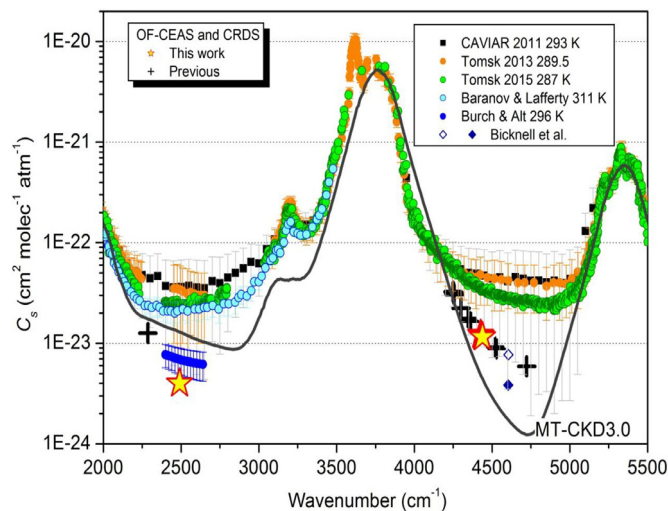
The absorption of light by water vapor manifests itself not only as rovibrational lines tabulated in standard spectroscopic databases like HITRAN [1] and GEISA [2] but also as a weak broadband absorption with a slow frequency dependence roughly following the rovibrational spectrum. Unlike in the strong absorbing regions where water vapor monomer lines dominate, in the regions of low absorption called “the water vapor transparency windows”, water vapor continuum absorption has a major contribution and may even dominate. Let us recall that the water self-continuum increases quadratically with the water number density and has negative temperature dependence and that, in the atmosphere, the continuum decomposes into a self-continuum component due to

water-water molecular interactions and a foreign-continuum due to water-nitrogen and water-oxygen interactions (see Ref. [3] for a recent review).

The default specification of the water vapor continuum is the semi-empirical MT\_CKD model (Mlawer-Tobin\_Clough-Kneizys-Davies) which is widely used in atmospheric radiative transfer codes and regularly updated (up to the V3.0 version very recently released) [4,5]. In the window regions, this semi-empirical model relies on far wing line shape theory. *Ad hoc* parameters have been constrained to laboratory and field measurements mostly in the far and mid-infrared [4,5]. In the mid- and near-infrared, the MT\_CKD continuum is then mostly an extrapolation which needs to be validated. The frequency dependence of the latest MT\_CKD continuum (V3.0) is presented in Fig. 1 for the  $2000\text{--}5500\text{ cm}^{-1}$  region together with an exhaustive collection of the available experimental results discussed below. As reviewed in Refs. [3,12], accurate laboratory measurements are lacking because of the difficulty of

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**Fig. 1.** Comparison of the MT\_CKD3.0 model (black solid line) [5] of the water vapor self-continuum cross-sections,  $C_s$ , in the 2000–5500  $\text{cm}^{-1}$  range to an exhaustive collection of experimental determinations: (i) FTS values reported by Baranov and Lafferty [6] (light blue circles), the CAVIAR consortium [7] (black full squares), from Tomsk2013 experiments [8] (orange full circles) and from Tomsk2015 experiments [9] (green full circles). The 30–50% error bars on Tomsk2015 FTS values [9] are not plotted for clarity; (ii) results by Bicknell et al. [10] from calorimetric-interferometry in air at 4605  $\text{cm}^{-1}$  (blue open diamond corresponds to a measurement in air, blue full diamond is an estimation of the self-continuum contribution [3]) (iii) measurements by Burch and Alt near 2500  $\text{cm}^{-1}$  using a grating spectrograph (solid blue circles) [11]; (iv) our previous measurements by CRDS [12,13] and OF-CEAS [12,14] (black crosses) and the present results at 2490  $\text{cm}^{-1}$  and 4435  $\text{cm}^{-1}$  (yellow stars). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

detecting the very small variation of the spectrum baseline (for instance on the order of  $10^{-8} \text{ cm}^{-1}$ ) induced by the injection of water vapor in an absorption cell. Indeed the continuum absorption retrieval by difference of the light intensities transmitted through the absorption cell in the absence and in the presence of water vapor requires very high baseline stability during the entire measurement period. Biases related to small changes in the alignment of the spectrometer, in the optical properties of the absorption cell (including the mirror reflectivity) have to be avoided. In our opinion, pressure squared dependence must be systematically used to insure the gas phase origin of the measured continuum absorption signals. In case of continuum retrieval from a unique spectrum recorded at a single pressure value, experimental biases related to the stability of the spectrometer or to the impact of water on the mirror reflectivity cannot be excluded. In the recent years, we have dedicated important experimental efforts to measure the self-continuum absorption of water vapor in the near infrared windows by implementing highly sensitive cavity-enhanced laser techniques at different spectral points of the 4.0, 2.1, 1.6 and 1.25  $\mu\text{m}$  windows [12–16]. Our previous results by Optical-Feedback Cavity-Enhanced Absorption Spectroscopy (OF-CEAS) [12,14] and Cavity Ring-down Spectroscopy (CRDS) [12,13] in the 4.0 and 2.1  $\mu\text{m}$  windows are summarized in Table 1 and included in Fig. 1. In all those measurements, the pressure squared dependence was carefully checked [12–16] using either pressure ramps or series of spectra recorded at different pressures. As discussed in Ref. [6,12], this was not the case of several recent studies by Fourier Transform Spectroscopy (FTS) with long path absorption cells which resulted in significantly larger values at room temperature in the transparency windows (see Fig. 1).

In the present work, we measure the water vapor self-continuum for two new spectral points: (i) the 2490  $\text{cm}^{-1}$  spectral point which corresponds to our second measurement in the

4.0  $\mu\text{m}$  window by OF-CEAS. The first measurement [12] located on the low energy edge of the window (2286  $\text{cm}^{-1}$ ) led to a self-continuum cross-section,  $C_s$ , about 30% lower than the corresponding MT\_CKD value and from two to four times lower than previous FTS values. The new 2490  $\text{cm}^{-1}$  spectral point is closer to the center of the 4.0  $\mu\text{m}$  window, (ii) The 4430  $\text{cm}^{-1}$  spectral point which fills a gap in our series of OF-CEAS and CRDS samplings in the low energy edge of the 2.1  $\mu\text{m}$  window (4249–4723  $\text{cm}^{-1}$ )— see Table 1.

The next two sections present for each of the two spectral points, the spectra acquisition, the continuum retrieval and a comparison to previous experimental and theoretical results.

## 2. OF-CEAS at 2490 $\text{cm}^{-1}$

OF-CEAS [17,18] is an alternative method to CRDS which was already used for water vapor self-continuum measurements in the 4.0 and 2.1  $\mu\text{m}$  windows [12,14]. The V-shaped geometry of the high-finesse cavity allows a part of the intra-cavity field to be re-injected in the diode-laser source. The resulting optical feedback towards the diode laser improves cavity injection by the laser radiation at the cavity mode frequencies [18]. OF-CEAS is able to generate several spectral scans per second of a small spectral region ( $\sim 1 \text{ cm}^{-1}$ ) containing few discrete absorption lines. The acquired spectra have then an intrinsically linear frequency scale with equally spaced spectral points separated by the cavity Free Spectral Range  $FSR=c/2nL$ , where  $c$  is the speed of light,  $L$  the effective cavity length, and  $n$  the refractive index of the intra-cavity sample.

Let us call  $H_{max}(m)$ , the maximum of the transmitted light at cavity mode  $m$  normalized to the reference laser power signal. The transmission spectra are obtained by multiplying the inverse square root of  $H_{max}(m)$  by a proportional factor ( $\beta$ ) [17]. This factor is the ratio of the effective mirror transmission coefficient,  $T$ , to the cavity length and can be determined from a measurement of the ring down time ( $\tau$ ) at the last mode ( $k$ ) of the laser scan [17,19]:

$$\beta = \frac{1}{\tau(k)c} \sqrt{H_{max}(k)} = \frac{T}{L} \quad (1)$$

In the present work, in order to average the scan-to-scan fluctuations of the  $\tau(k)$  values, an averaged value of  $\beta$  was used for all the measurements of a given pressure ramp. In fact while  $\tau(k)$  and  $H_{max}(k)$  both decrease with pressure due to continuum absorption and to wings of discrete absorption lines (which become broader with pressure), the resulting normalization factor  $\beta$  does not change as expected from Eq. (1). In practice, this factor depends only on slowly drifting parameters such as mirror transmission, photodiodes gain and optomechanical alignment. It was indeed experimentally verified that the value of  $\beta$  does not evolve during a pressure scan, which confirmed the adequacy of using an averaged value to reduce noise in the determination of the evolution of spectral baseline versus pressure. The averaged  $\beta$  value was determined with a typical 0.2% accuracy by averaging about 800 determinations over a few minutes.

### 2.1. Spectra acquisition and self-continuum cross-section retrieval

The OF-CEAS spectrometer used in this work is similar to that presented in [14]. The reader is referred to that paper (in particular its Fig. 1) for a detailed description. In the present experiment, an Interband Cascade Laser (ICL) emitting around 2491  $\text{cm}^{-1}$ , designed by Nanoplus GmbH was used. Each arm of the V-cavity had a length of about 400 mm resulting in an effective length of 800 mm and a  $FSR=187.5 \pm 0.5 \text{ MHz}$ . At the laser wavelength, the reflectivity of the cavity mirrors (from LohnStar Optics) was 99.981%, as

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