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The self- and foreign-absorption continua of water vapor by cavity ring-down spectroscopy near 2.35 μm

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Number of Pages: 18

Number of Figures: 10

Number of Tables: 3

Keywords:

water vapor continuum, self-continuum, foreign-continuum, CRDS, transparency window, MT-CKD continuum

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Abstract

The room temperature self- and foreign-continua of water vapor have been measured near 4250 cm^{-1} with a newly developed high sensitivity Cavity Ring Down Spectrometer (CRDS). The typical sensitivity of the recordings is $\alpha_{\min} \approx 6 \times 10^{-10}\text{ cm}^{-1}$ which is two orders of magnitude better than previous FTS measurements in the spectral region. The investigated spectral interval is located in the low energy range of the important $2.1\text{ }\mu\text{m}$ atmospheric transparency window. Self-continuum cross-sections, C_s , were retrieved from the quadratic dependence of the spectrum base line level measured for different water vapor pressures between 0 and 15 Torr, after subtraction of the local water monomer lines contribution calculated using HITRAN2012 line parameters. The C_s values were determined with 5 % accuracy for four spectral points between 4249.2 and 4257.3 cm^{-1} . Their values of about $3.2 \times 10^{-23}\text{ cm}^2\text{ molecule}^{-1}\text{ atm}^{-1}$ are found 20 % higher than predicted by the MT_CKD V2.5 model but two times weaker than reported in the literature using Fourier Transform Spectroscopy (FTS).

The foreign-continuum was evaluated by injecting various amounts of synthetic air in the CRDS cell while keeping the initial water vapor partial pressure constant. The foreign-continuum cross-section, C_f , was retrieved from a linear fit of the spectrum base line level *versus* the air pressure. The obtained C_f values are larger by a factor of 4.5 compared to the MT_CKD values and smaller by a factor of 1.7 compared to previous FTS values.

As a result, for an atmosphere at room temperature with 60% relative humidity, the foreign-continuum contribution to the water continuum near 4250 cm^{-1} is found to be on the same order as the self-continuum contribution.

1. Introduction

The atmospheric transparency windows, corresponding mainly to spectral intervals of weak water vapor absorption, are used for atmospheric remote sensing [1] and for quantifying the contribution of geophysical elements with spectrally large optical signature like surface albedoes [1], clouds [2] and aerosols. In the infrared atmospheric windows, between 2000 and 9000 cm^{-1} , absorption is believed to be dominated by the water vapor continuum contribution [3] which thus requires accurate determination for atmospheric applications. Water vapor continuum and its large uncertainty also impact radiative transfer calculations leading to a dominant uncertainty compared to uncertainty due to the other spectral data involved in the calculations [4].

The usual definition of the water continuum is somewhat arbitrary as it relies on an arbitrary separation of the contributions of the water local monomer line (WML) and of the absorption continuum. The water continuum is defined as the difference between the measured absorption spectrum and the sum of the monomer absorption lines. This WML sum is obtained by adding the Voigt profile of the different absorption lines calculated within $\pm 25 \text{ cm}^{-1}$ from the line center but without the “plinth term”, corresponding to the absorption of the line at $\pm 25 \text{ cm}^{-1}$ from the line center, which is considered as part of the continuum [3]. The HITRAN line list is used as reference for these WML calculations. The reported continuum values are then dependent of the version and of the quality of the HITRAN database used. This aspect should be kept in mind in particular in the near infrared transparency windows for which the HITRAN line list may present deficiencies [5]. Note that, in the following, the self- and foreign-continuum designate the continuum contributions due to interactions between water molecules, and between water molecules and other atmospheric molecules, mainly nitrogen and oxygen, respectively.

After more than one century from its experimental discovery [6,7], the physical origin of the water continuum is still an open question [see the recent reviews in 8 and 9]. Two main physical processes are believed to contribute to the water absorption continuum:

- (i) Far-wings of the absorption lines of the monomer [10] and more generally the monomer line shape perturbations due to pair collisions, and
- (ii) Molecular association *i.e.* bound and quasi-bound water dimers [11,12].

In this situation, a pragmatic approach is widely adopted in radiative transfer codes which use the so-called MT_CKD model [13] which is a semi-empirical formulation of the continuum. This model includes a “weak interaction term” and an “allowed term”, in which the far wings of the water vapor monomer line profiles are sub-lorentzian with a wavenumber dependent χ factor. In these two contributions, additional *ad hoc* parameters are adjusted to account for validated atmospheric and laboratory measurements. These experimental constraints are mainly in the microwave and mid-infrared regions (*i.e.* the 10 μm window) and for the 2.5 version in the near infrared region with the studies of Bicknell et al [14] and Fulghum and Tilleman [15]. Taking into account the increase of the actinic flux in the near infrared, the test of the MT_CKD continuum in the near infrared range is of importance for atmospheric sciences.

Recently, the CAVIAR (Continuum Absorption at Visible and Infrared wavelengths and its Atmospheric Relevance) consortium reported the self- and foreign-continuum cross-sections in four transparency windows between 1 and 5 μm . These measurements were performed at the Rutherford Appleton Laboratory (RAL) using a Fourier transform spectrometer (FTS) coupled to different multi-pass absorption cells [3,16]. In the center of the studied transparency windows, the CAVIAR self-continuum cross-sections, C_s , are typically one order of magnitude higher than obtained using the MT_CKD V2.5 model [13]. This discrepancy is even larger -up to two orders of magnitude- for the foreign-continuum cross-sections, C_f [16]. If they are confirmed, these larger foreign-continuum cross-sections compared to MT_CKD V2.5, would lead to a significant increase of the atmospheric absorption of solar radiation. An additional global-averaged value of about 0.46 W m^{-2} was reported in [16] for clear sky conditions.

Very recently, room temperature FTS measurements of the self continuum performed at IAO-Tomsk [17] confirmed CAVIAR results in the 4.0 and 2.1 μm windows and extended the measurements to the 1.6 and 1.25 μm windows. Discrepancies up to two orders of magnitude with

the widespread MT_CKD V2.5 model were noted in these windows (CAVIAR measurements were not reported at room temperature in the 1.6 and 1.25 μm windows).

Prior to these FTS studies, using a calorimetric–interferometric method, Bicknell *et al.* [14], reported a total (self plus foreign) water vapor continuum cross-section significantly smaller than the above FTS values but still nine and three times larger than the MT_CKD values around 1.63 and 2.17 μm , respectively.

The disagreement between various measurement data-sets motivated our investigation of the water self continuum in the 1.6 μm window using an alternative and more sensitive experimental approach [18,19]. Compared to FTS which requires longer acquisition times, laser techniques such as Cavity Ring Down Spectroscopy (CRDS) have the advantage of providing real time measurements at a chosen wavelength when experimental parameters (pressure, gas composition...) are varied. Our self continuum cross-sections were obtained for ten selected wavenumbers between 5875 and 6665 cm^{-1} . The CW-CRDS absorption coefficients were measured in real time during pressure ramps. The derived C_s values range between 1.5×10^{-25} and $2 \times 10^{-24} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$ with a minimum around 6300 cm^{-1} . While a reasonable agreement (within 50 %) was observed over the whole window with the cross-sections provided by the MT_CKD V2.5 model, our values are considerably smaller than the FTS values of Ref. [17] which are mostly constant ($3.5 \pm 2 \times 10^{-23} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$) for the whole 1.6 μm window.

In the 2.1 μm window, a similar large discrepancy exists between the MT_CKD and CAVIAR self continuum cross-section values. The aim of the present work is to develop a new CRDS spectrometer to access this spectral window and measured the self- and foreign- continua by CRDS at room temperature. The CRDS experimental set-up is described in the next Section 2, the measurements and the procedure applied to retrieve the cross-sections from the measured spectra will be detailed in Section 3. The comparison with the literature will be discussed in Section 4 before concluding remarks and perspectives (Section 5).

2. CRDS measurements near 2.35 μm

2.1. The cavity ring down spectrometer

The spectra were recorded with a newly developed high sensitivity cavity ring down spectrometer. Even if high sensitivity techniques such as ICLAS [20] and OF-CEAS [21] have already been developed in the 2.3 μm region, to the best of our knowledge, only one pulsed-CRDS experiment has been previously reported in this region with a limited detection sensitivity of the order of $2.0 \times 10^{-7} \text{ cm}^{-1}$ [22]. This restricted number of experimental developments is probably related to technical limitations such as less powerful and non-fibered laser sources, less sensitive detectors and availability of elements adapted for this spectral region. The CRD spectroscopy technique [23,24,25] allows to determine the extinction coefficient, $\alpha(\nu)$ (in cm^{-1}), at a wavenumber ν , from the measured cavity ring-down times, τ and τ_0 , when the cell is filled and is evacuated, respectively:

$$\alpha(\nu) = \frac{1}{c\tau(\nu)} - \frac{1}{c\tau_0(\nu)} \quad (1)$$

Where c is the speed of light (neglecting the refractive index of the gas, very close to 1).

Our spectrometer presented Figure 1 uses as light source a Distributed Feed Back (DFB) laser diode (from Nanoplus) which can be frequency tuned between 4248.8 and 4257.3 cm^{-1} by changing its temperature step by step from 18°C to 40°C, the laser current being fixed. About 10% of the emitted light is sent into a wavemeter (Model 621-A IR from Bristol) for a direct measurement of the laser wavelength. The main part of the beam is coupled into a single mode fluoride fiber for spatial filtering and then sent through a 1.4 meter long high-finesse cavity ($F \approx 78000$). Resonance between the laser light and a longitudinal mode of the cavity is achieved by changing the cavity length over one Free Spectral Range (FSR) thanks to the rear mirror of the cavity mounted on a Piezoelectric Transducer (PZT). At resonance, the injection of the laser beam into the cavity is interrupted with an acousto-optic modulator (Model ACM-1002AA1 from IntraAction Corp.) and a ring-down time is measured with an InGaAs PIN photodiode. Typically 15 ring downs are averaged at each spectral

point leading to a minimum detectable absorption coefficient, $\alpha_{\min} \approx 6 \times 10^{-10} \text{ cm}^{-1}$. Sampling steps of $2 \times 10^{-3} \text{ cm}^{-1}$ and $5 \times 10^{-3} \text{ cm}^{-1}$ are used for pure water and air plus water spectra, respectively, leading to typical recording durations of 15 and 40 min. Note that two optical isolators are placed just in front of the laser diode to avoid perturbations of the laser due to back reflections.

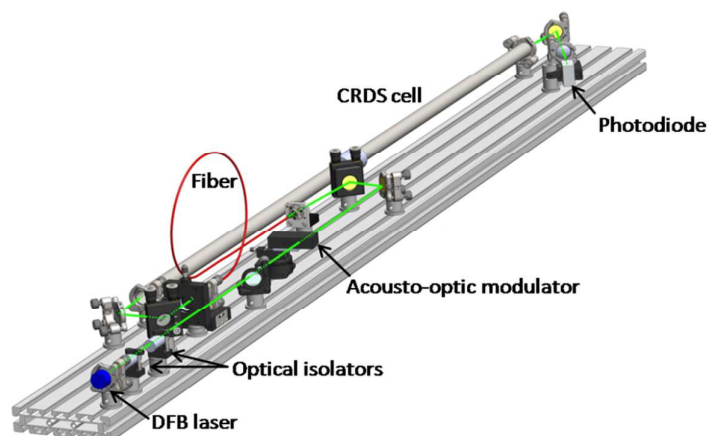


Figure 1. Three-dimensional view of the CRDS spectrometer. The infrared beam trajectory is marked by the green line.

2.2. Data acquisition

At the beginning of each day of measurements, the water sample is purified by cooling with liquid nitrogen and pumping on the residual vapor phase. For the determination of the self-continuum cross-section, several tens of spectra were recorded with the CRDS cell filled with different pressures of pure water up to 15 Torr (about 71% of the saturation pressure at 296 K). The pressure was continuously monitored and recorded either with a 1 Torr or a 100 Torr absolute pressure transducer (accuracy: 0.25% of reading) depending of the filling pressure. Figure 2 shows the evolution of the CRDS spectra for different pressures of water vapor between 2 and 15 Torr.

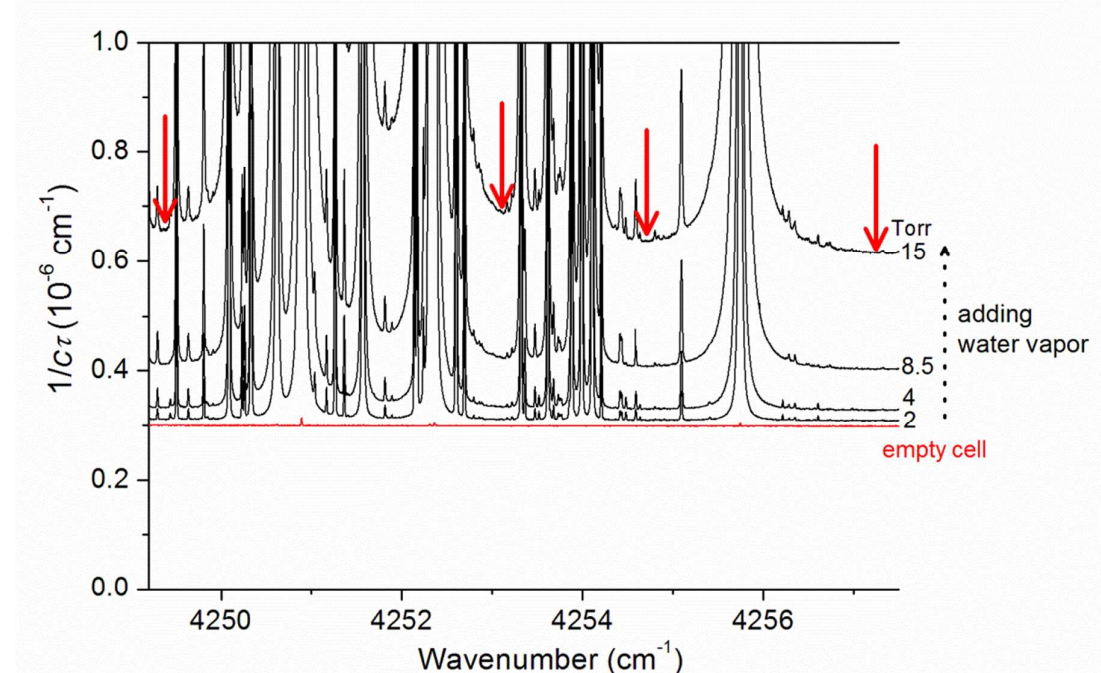


Figure 2. Series of CRDS spectra recorded with our DFB based-CRD spectrometer for different pressures of pure water vapor up to 15 Torr. The red arrows indicate the spectral points where the self-continuum measurements were performed.

The cell temperature was measured with a temperature sensor (TSic 501, IST-AG, ± 0.1 K accuracy) fixed on the cell surface, covered by an external blanket for thermal isolation. During all the recordings reported here, the cell temperature varied between 296.5 and 298.5 K.

For the foreign-continuum measurements, the cell was first filled with a certain pressure of pure water and once stabilized, synthetic air (Alphagaz 2 from Air Liquide) was added into the cell to reach the desired total pressure. As illustrated in Figure 3, for a given value of the water partial pressure, several spectra were recorded with increasing amounts of air added, corresponding to 4 or 5 pressure values between 150 and 700 Torr.

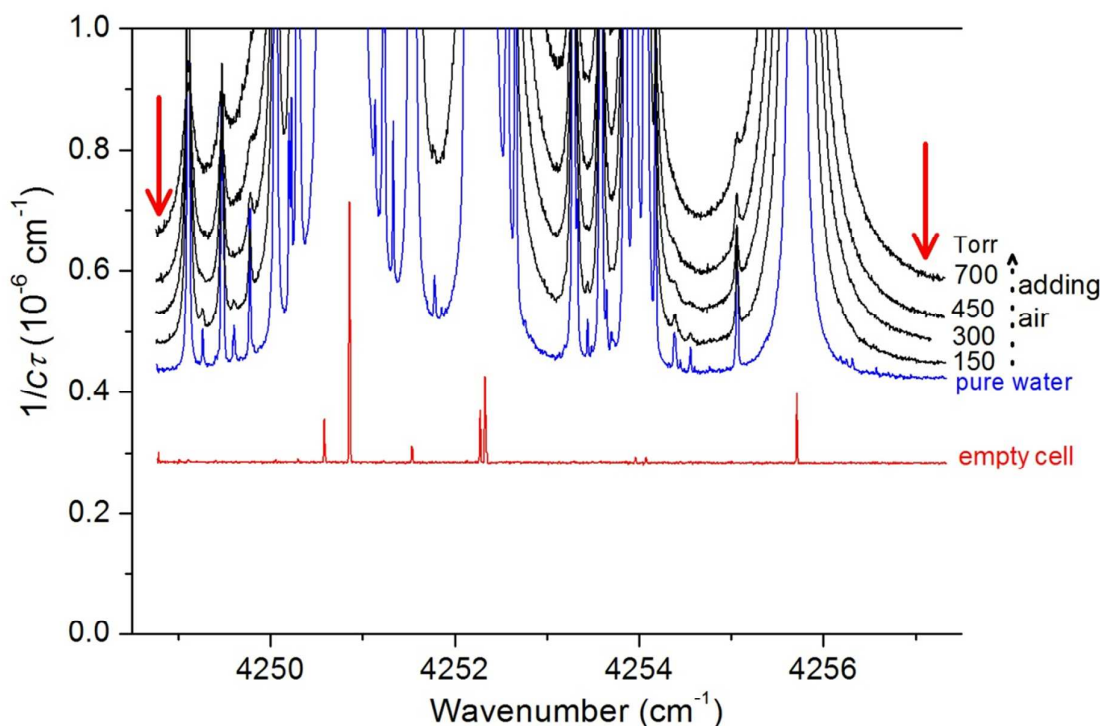


Figure 3. Series of CRDS spectra recorded by adding air into the CRDS cell containing water at a partial pressure of 9.65 Torr. The total pressure is increased up to 700 Torr. The red arrows indicate the two spectral points where the foreign-continuum measurements were performed.

3. Cross-section retrievals

When the CRDS cell is filled with water vapor and air, the extinction coefficient can be expressed as a sum of three terms:

$$\alpha(\nu) = \alpha_{WML} + \alpha_{WC} + \alpha_{Ray} \quad (2)$$

where α_{WML} , α_{WC} and α_{Ray} are the contributions due to water vapor - monomer local lines (WML) and continuum (WC) - and Rayleigh scattering, respectively. Note that in our measurements near $1.6 \mu\text{m}$, we observed an additional contribution proportional to the water vapor pressure which was interpreted as due to water molecules adsorbed on the mirror surfaces [18]. In the present work, no indication of such a linear contribution was found and a pure quadratic dependence with the pressure was observed for the self-continuum measurements (see below).

3.1 Rayleigh scattering contribution

The Rayleigh scattering contribution can be calculated from the refractive index (see Eq. 1 in Thalman *et al* [26]). In the present work, we used the longitudinal modes scrolling with pressure to measure accurately the value of the refractive index (n) at 4257 cm^{-1} for pure water and air. We

obtained $n = 1.000005$ for 15 Torr of water vapor and $n = 1.000296$ for 760 Torr of air at 296.6 K, leading to Rayleigh scattering contribution $\alpha_{Ray} = 5 \times 10^{-12} \text{ cm}^{-1}$ and $3 \times 10^{-10} \text{ cm}^{-1}$, respectively. We note that our measured value of the refractive index of water vapor at 4257 cm^{-1} is consistent with the value of 1.000006 given in [27] at 4300 cm^{-1} (298.15 K; 24 Torr).

Considering that in our experimental conditions, the water continuum induces variation of the spectrum base line on the order of 10^{-8} - 10^{-6} cm^{-1} , we conclude that the Rayleigh scattering contribution can be neglected.

3.2 Water monomer local line contribution

As indicated in the Introduction, the water monomer local line contribution to be subtracted from the CRDS spectrum is a spectrum simulation in the experimental conditions of the recordings, based on the water list provided in the HITRAN2012 database [28]. Following [13], a Voigt profile is calculated over a $\pm 25 \text{ cm}^{-1}$ interval from the line center and reduced by the value of the "25 cm^{-1} plinth". The measured temperature of the recordings was used to extrapolate the line intensities from their 296 K value provided in the HITRAN database. Figure 4 (right panel) illustrates the good agreement between the local line simulation and the measured spectrum in the case of 9.65 Torr partial pressure of water in air at a total pressure of 700 Torr: the experimental spectrum coincides with the local line monomer spectrum shifted up by a constant value corresponding to the continuum (which includes in that case both a self and a foreign contribution).

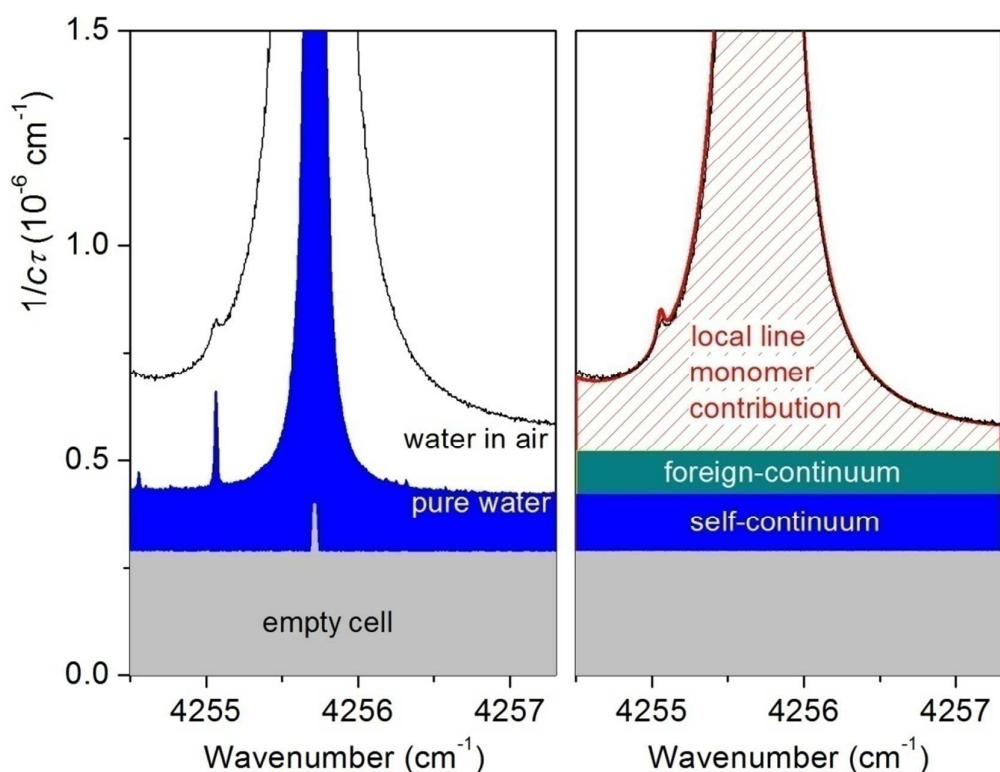


Figure 4. Illustration of the procedure used to derive the foreign-continuum contribution near 4256 cm^{-1} . Left panel: evolution of the CRDS spectrum by adding successively 9.65 Torr of water vapor and air up to a total pressure of 700 Torr. Right panel: Evaluation of the foreign-continuum contribution (dark cyan) by difference of the absorption signal with the sum of the water monomer local line contribution (dashed) and self-continuum contribution (blue).

3.3 Cross-section retrievals

The continuum absorption coefficient of water vapor in air, α_{WC} , obtained after subtracting the monomer local lines from the extinction coefficient is the sum of the self and foreign contributions (Figure 4)

$$\alpha_{WC}(\nu, T) = \alpha_{WCS}(\nu, T) + \alpha_{WCF}(\nu, T) = \frac{1}{k_B T} C_S(\nu, T) P_{H_2O}^2 + \frac{1}{k_B T} C_F(\nu, T) P_{H_2O} P_F \quad (3)$$

Where k_B is the Boltzmann constant, T is the temperature in K, P_{H_2O} is the water vapor partial pressure, and P_F is the foreign gas (here air) partial pressure in atm. C_S and C_F represent the self- and foreign-continuum cross-sections, respectively, and are expressed in $\text{cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}$ at a given temperature T , following the definition in Burch and Alt [29]. Note that for comparison, the MT_CKD values which are normalized to the number density at 1 atm and 296 K, should be multiplied by the factor $296/T$ [30].

Self continuum

Figure 2 shows spectra recorded with the CRDS cell filled with pure water at different pressures from 2 to 15 Torr. For the four spectral points chosen, the calculated local line monomer absorption, α_{WML} , is found to have relative contribution ranging between 5 and 20 % (see Table 1). As illustrated in Figure 5, the water self continuum, α_{WC} , obtained after subtraction of α_{WML} shows a purely quadratic pressure dependence. The C_S cross-section values listed in Table 1, were derived from the fitted value of the quadratic coefficient of $\alpha(\nu, T)$ versus the water pressure.

Table 1. Self-continuum absorption cross-sections of water at 298 K and relative contribution of the monomer local lines for the different selected spectral points.

ν cm^{-1}	C_S $10^{-23} \text{ cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}$	$\alpha_{WML}/(\alpha_{WML} + \alpha_{WC})$ %
4249.36	3.26(3)	13
4253.12	3.21(3)	20
4254.66	3.12(3)	10
4257.30	3.04(2)	5

Note

The error bar is given in parenthesis in unit of the last quoted digit. It corresponds to the statistical uncertainty on the quadratic coefficient of the fit of the continuum versus the water vapor pressure.

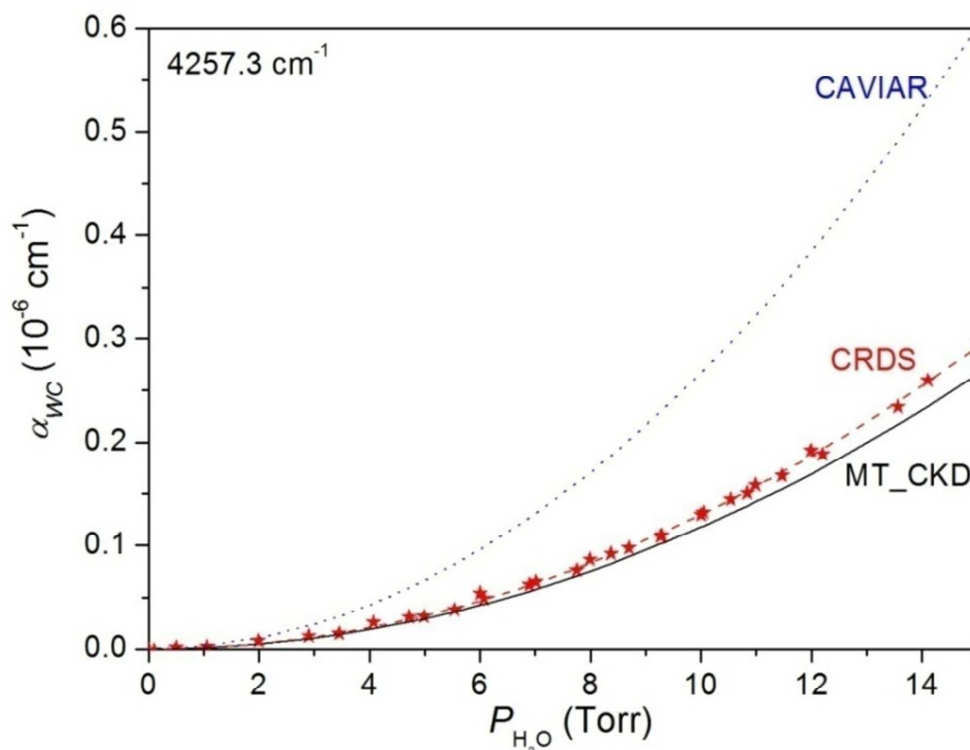


Figure 5. Pressure dependence of the water self-continuum absorption at 4257.3 cm^{-1} . The values presently measured by CRDS at 297.9 K (red stars) are compared to those calculated from the C_s cross-sections measured in Ref. [3] by FTS at 293 K (dotted line) and provided by the MT_CKD V2.5 model (black solid line). The red dashed line corresponds to a purely quadratic polynomial fit of the CRDS data (RMS value of the residuals of $2.8 \times 10^{-9} \text{ cm}^{-1}$).

Foreign continuum

Figure 3 shows one of the series of the recordings performed to determine the foreign-continuum. Various amounts of synthetic air are successively injected into the CRDS cell initially filled with water vapor at a pressure of $P_{H_2O} = 9.65 \text{ Torr}$, leading to total pressure values of $P_{H_2O} + P_F = 150, 300, 450$ and 700 Torr . The injection of air is accompanied by an additional increase of the spectrum base line due to both water monomer local lines broadened by air (α_{WML}) and the foreign continuum contribution (α_{WCF}). The different contributions are highlighted in Figure 4. The α_{WML} contribution subtracted represents a more important part of the measured absorption (see Table 2) compared to the self-continuum case. Note that far from the line center, α_{WML} is roughly proportional to the air partial pressure (P_F). The value of the foreign continuum absorption coefficient (α_{WCF}) is then the spectrum base line shift of the air + water mixture from its level measured with the cell evacuated, decreased by the α_{WML} and self continuum contributions at the given water partial pressure (Figure 4). Figure 6 shows the pressure dependence of the foreign and local line contributions at 4257.3 cm^{-1} . As expected from Eq. (3), α_{WCF} is proportional to P_F . The foreign-continuum cross-sections were obtained at 4248.83 and 4257.30 cm^{-1} from the fitted value of the proportionality factor, $\frac{1}{k_B T} C_F(\nu, T) P_{H_2O}$. The C_F values derived from series of recordings performed with different partial pressures of water are listed in Table 2.

It is worth mentioning that the exclusion of the plinth from the continuum has a negligible impact on the self-continuum due to the low water vapor pressures used and a limited impact on the derived foreign continuum (below a few percent of the total continuum).

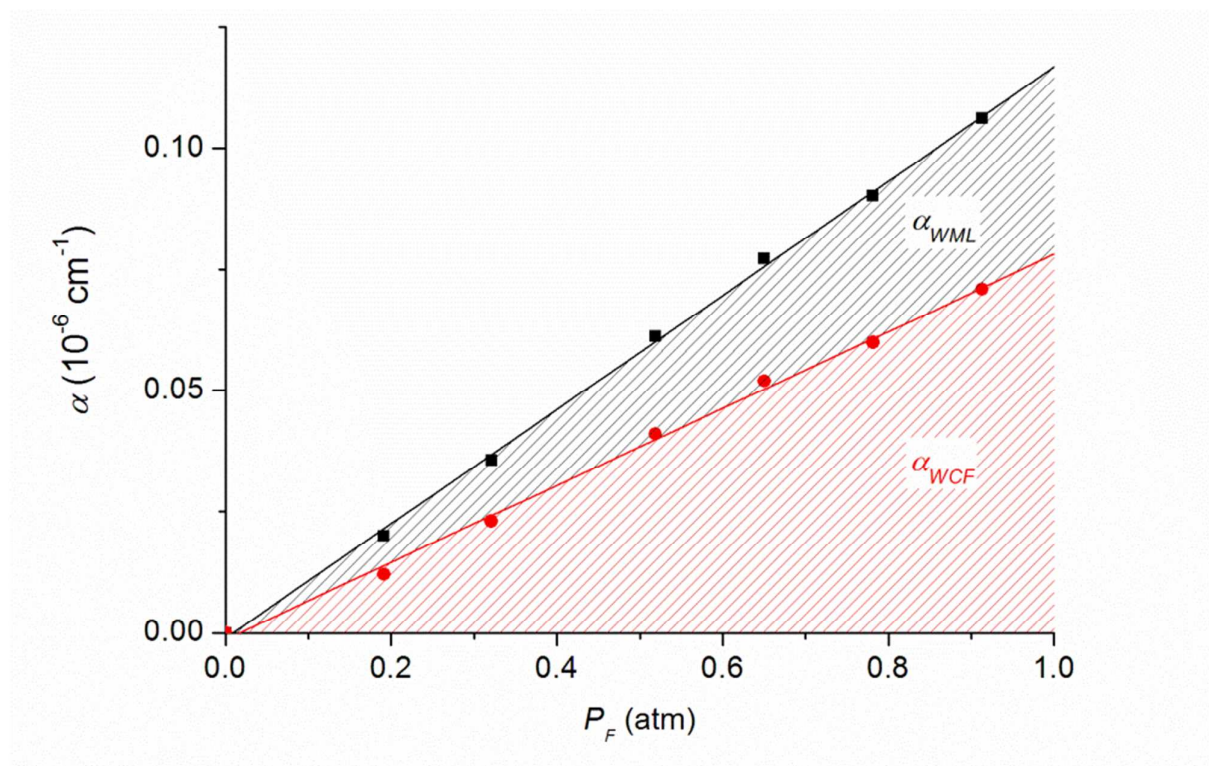


Figure 6. Pressure dependence of the total (black squares) and foreign-continuum (red circles) absorption at 4257.3 cm^{-1} measured in this work by CRDS. Lines correspond to the linear fit of the CRDS data. The respective contributions of the foreign-continuum, α_{WCF} , and of the calculated monomer local lines, α_{WML} , are also shown.

Table 2. Foreign-continuum cross-sections measured by CRDS at 297 K and relative contribution of the monomer local lines for the different selected spectral points. For a given spectral point, the cross section value was derived for several values of the water partial pressure.

ν cm^{-1}	$P_{\text{H}_2\text{O}}$ Torr	C_F $10^{-25} \text{ cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}$	$\alpha_{WML}/(\alpha_{WML} + \alpha_{WCF})$ %
4248.83	4.0	4.42(23)	50
	6.2	4.24(10)	53
	9.7	3.57(11) 3.91(40) ^a	55
	9.8	3.80(11)	55
	10.9	3.75(16)	56
4257.30	4.0	4.26(19)	31
	6.2	3.93(9)	33
	9.7	3.82(20) 3.93(30) ^a	34
	9.8	3.60(23)	34

Note.

The error bar is given in parenthesis in unit of the last quoted digit. It corresponds to the statistical uncertainty on the coefficient of the linear fit of the continuum versus the air pressure.

^a Weighted average.

3.4 Estimated uncertainties

We have included in Tables 1 and 2 the statistical error given by the quadratic (C_S) or linear (C_F) fit of α_{WC} versus $P_{\text{H}_2\text{O}}^2$ and P_F , respectively. As illustrated on Figs. 5 and 6, the quality of the reproduction of the pressure dependence is very good, in particular for the self continuum for which we obtain a 1 % error bar for the four chosen spectral points. The quality of our C_S values is

confirmed by the frequency dependence included as an insert in Fig. 7. Although the extreme measurement points are separated by no more than 8 cm^{-1} , a clear decrease with the frequency is evidenced. Interestingly, this C_S frequency dependence is very similar to that predicted by the MT_CKD model.

The above statistical error of the fits represents only a part of the real error bar. Experimental and data treatment biases or errors may also contribute to the uncertainty budget on our C_S and C_F values. Among the additional error sources, we identified those related to (i) the stability of the spectrum base line (ii) the uncertainty on the calculated contribution of the monomer local lines and (iii) the stability of the partial pressure of water in the air + water mixture used for the foreign continuum measurements.

All our cross-section retrievals rely on the assumption that the optical alignment of the CRDS cavity and then the base line of the spectra are not affected by pressure changes accompanying the cell filling. In order to estimate to which extent the cavity is mechanically stable, we recorded a series of spectra with Ar or (dry) synthetic air at pressure up to 700 Torr. Up to 200 Torr (in particular in pressure conditions similar to those of the self continuum measurements) the base line variations were found at the noise level ($< 10^{-9}\text{ cm}^{-1}$) and then negligible compared to the typical changes induced by the injection of water on the order of 10^{-8} - 10^{-7} cm^{-1} . At higher pressures, a small misalignment of the mirrors was nevertheless noted resulting, after realignment, in an increase of the base line level never exceeding $7 \times 10^{-9}\text{ cm}^{-1}$ at 700 Torr compared to the empty cell level.

As mentioned above, our cross-section retrieval uses the water list provided in the HITRAN2012 database to calculate the monomer local line contribution (α_{WML}). Note that the calculation of α_{WML} includes the contribution of lines located 25 cm^{-1} below and above the range of our CRDS recordings. Even if the overall agreement between our spectrum and the HITRAN simulation is good (see Figure 4), the achieved CRDS sensitivity allowed evidencing a number of minor deviations and missing weak lines compared to the HITRAN simulation. The impact of these deviations will be quantified after construction of a new experimental line list in this spectral region but is expected to be limited in particular on the self-continuum cross section for which α_{WML} represents a smaller relative contribution (see Table 1 and 2).

Our C_F values rely on series of spectra of water vapor in air recorded for various partial pressures of water vapor at 4248.83 and 4257.30 cm^{-1} (Table 2). In order to insure that the water partial pressure was not affected during the air injection, the pressure of the synthetic air admission line was kept at a high value. In order to check that the water partial pressure was not impacted by a variation of the amount of water adsorbed on the CRDS cell, we determined the water vapor partial pressure from the fitted value of the profile area of three lines. For a given series, the water pressure values were found to be constant within $\pm 7\%$.

Taking into account the various sources of error (base line stability, HITRAN line parameters, 7 % dispersion of the water vapor partial pressure in a series of recordings, statistical dispersion of the measurements) we give a 30% error bar on our C_F values as an estimate of our real uncertainty. This value may be reduced after the construction of an improved line list for water in the region with particular attention to the pressure broadening coefficients and to the lines due to the minor water isotopologues which have an important contribution in the region.

In the case of the self continuum cross section, taking into account the high consistency of the various measurements performed and the smaller impact of the baseline and α_{WML} uncertainties, a 5 % error bar seems to be a conservative estimate. Our recommended C_S and C_F values at 4250 cm^{-1} are listed in Table 3 with their estimated error bar and compared to the other values available in the literature in the same spectral region.

Table 3. Comparison of the self- and foreign-cross sections at 4250 cm^{-1} measured in this work with the values available in the literature. The error bar is given in parenthesis in unit of the last quoted digit.

C_s ($10^{-23}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$)			
This work	MT_CKD2.5 [13]	CAVIAR [3]	Ptashnik et al [17]
3.26(16)	2.74	6.2(39)	5.7(24)
C_F ($10^{-25}\text{ cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$)			
This work	MT_CKD2.5 [13]	CAVIAR [16]^a	
3.9(13)	0.87	6.8(22)	

Note.

^a C_F value reported in Ref. [16] at 402 K and 4260 cm^{-1} , multiplied by the factor 296/402 for conversion to the $\text{cm}^2\text{ molec}^{-1}\text{ atm}^{-1}$ unit (see Eq. (3))

4. Discussion

4.1. Self-continuum cross-sections

Our measured C_s values are a factor of about 2 and 1.8 smaller than the FTS C_s cross-sections reported in Ref. [3] and [17], respectively, but are consistent within the 63 and 42 % error bars of the FTS measurements, respectively. These data together with our previous CRDS measurements in the $1.6\text{ }\mu\text{m}$ window [19] are gathered in Figure 7. A much better agreement is observed with the MT_CKD model with a difference less than 20%, our values being systematically higher. Similarly to the situation encountered in the $1.6\text{ }\mu\text{m}$ region, the present measurements near $2.35\text{ }\mu\text{m}$ confirm the MT_CKD values of the self-continuum cross-sections at room temperature. As mentioned above, the C_s frequency dependence measured by CRDS over a 8 cm^{-1} interval further support the MT_CKD values (insert of Fig. 7).

In the same figure, results obtained by Bicknell *et al.* [14] at 4605 cm^{-1} for a nitrogen plus water vapor mixture are also displayed. The absorption measured in this latter work corresponds to the sum of the self- and foreign-continuum. If we consider that all this absorption is due to the self-continuum, an upper limit is obtained for the retrieved self-continuum cross-section (open diamonds in Figure 7) (see also Ref [17] for discussion). But if, following our results (see below), the foreign-continuum contributes to the same level than the self-continuum (for 15 Torr of water vapor and 760 Torr of air), the Bicknell's C_s values is two times smaller (full diamonds in Figure 7). We nevertheless note that, in spite of their large error bars, the Bicknell's C_s values at 4605 cm^{-1} are in disagreement with both the MT_CKD model and the data of Refs [3,17].

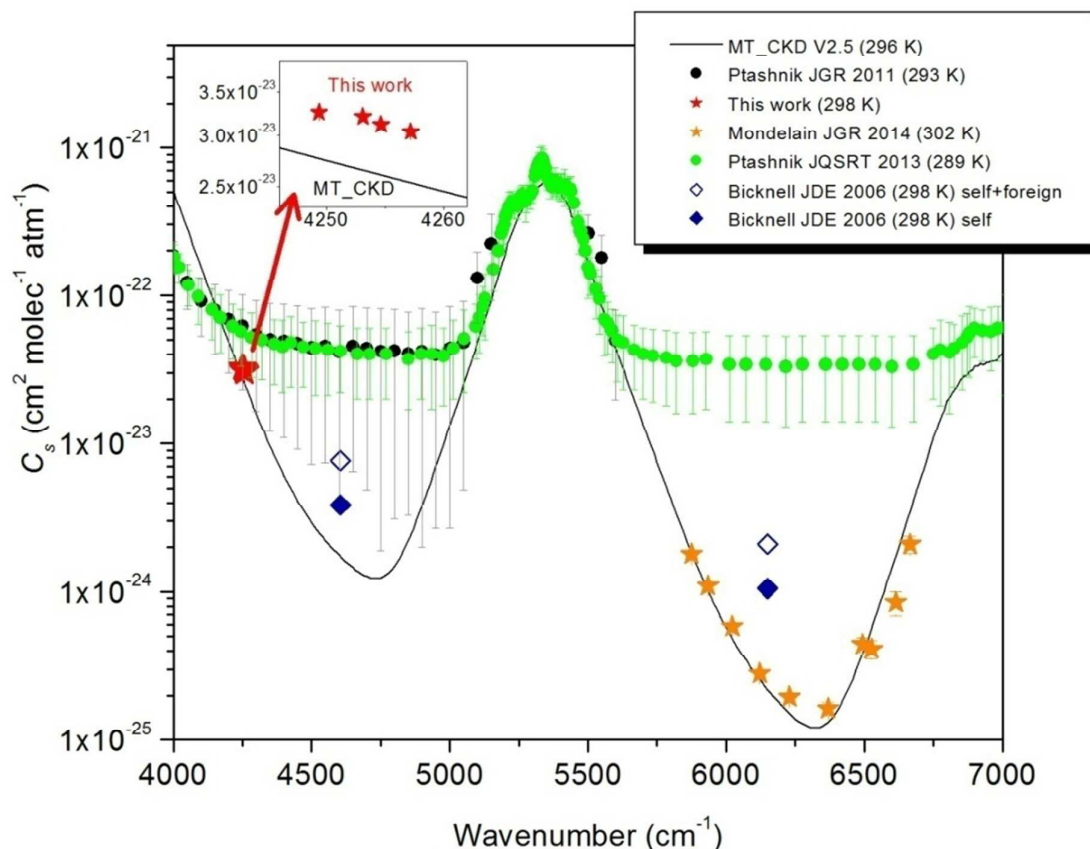


Figure 7. Spectral dependence of the self-continuum cross-section, C_s , at room temperature derived from the MT_CKD V2.5 model [13] (black solid line) and measured in Refs [3] (black circles), [17] (green triangles), [19] (orange stars), [14] (blue diamond's) and in this work (red stars). Note the logarithmic scale adopted for the ordinate axis.

In Ref. [3], the CAVIAR consortium measured the self-continuum cross-sections at 293 K with a long-path absorption cell ($l = 512.7$ m) and at temperatures from 350 K to 472 K with a short-path absorption cell ($l = 17.7$ m). The CAVIAR cross-sections measured at different temperatures and our present C_s values at 298 K are plotted in Figure 8 together with the MT_CKD values at 4250 cm^{-1} . As in Ref. [3], we use a logarithmic scale for the cross section and plot them versus $1/T$. Interestingly, the CAVIAR high temperature C_s values extrapolated linearly to room temperature coincide much better to our room temperature value than to CAVIAR 293 K value. We noted the same kind of situation in the edges of the 1.6 μm window (see Figure 8 of Ref [19]). This may be due to the fact that optical depth of the high temperature measurements are much larger than those at room temperature, because of the larger amount of water vapor possible in the cell allowing for more accurate FTS measurements. Nevertheless, large uncertainties remain on the temperature dependence of the water continuum in the transparency windows. For instance, in the considered 2.3 μm window, the temperature dependence provided by the MT_CKD model differs from the CAVIAR high temperature results as seen on Figure 8. Let us recall that the MT_CKD model is mainly constrained on atmospheric spectra *i.e.* to temperature values close to or lower than room temperature so that its extrapolation capabilities at higher temperature may be questioned.

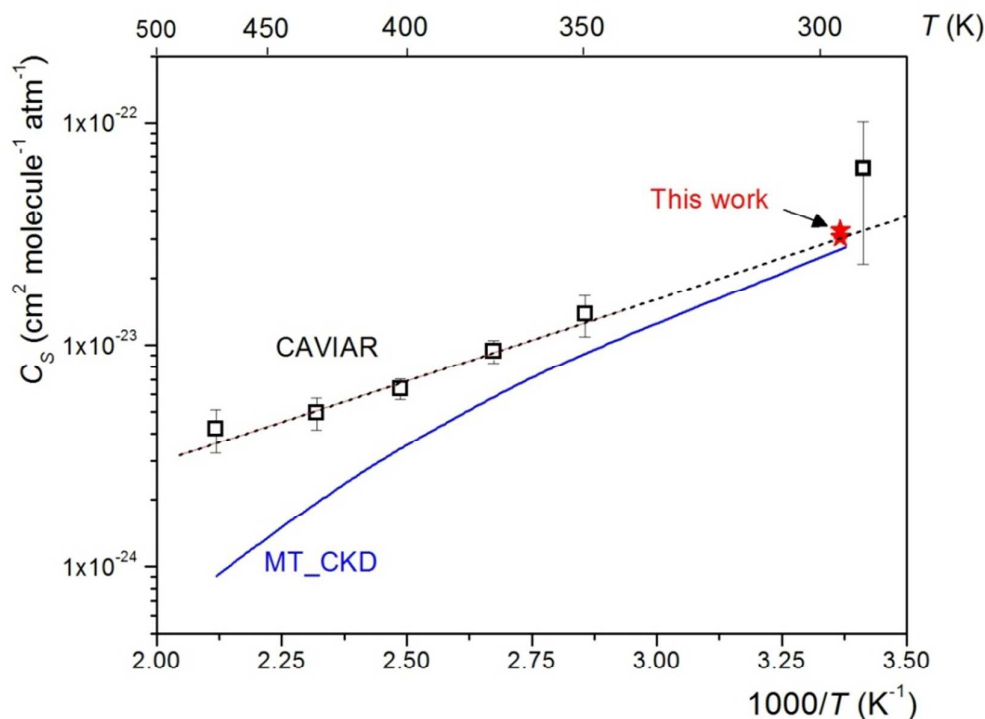


Figure 8. Temperature dependence of the water self-continuum cross sections, C_s , obtained by CRDS at 297 K (red stars), from Ref. [3] (black squares) and from the MT_CKD V2.5 model (blue solid line) at 4250 cm^{-1} . The MT_CKD values take into account of the $296/T$ correction factor (see Text). Data of Ref. [3], without the 293 K data point (black squares), are linearly extrapolated to room temperature (black dotted line).

4.2 The foreign-continuum cross-sections

Our cross-sections are about 4.5 times higher than the MT_CKD V2.5 values at 296 K, and about 1.7 times lower than the only numerical value reported by the CAVIAR consortium which is for $T = 402\text{ K}$ [16] (Figure 9). Note that according to Fig. 4 of [16], the temperature dependence of the foreign-continuum cross-sections between 350 and 431 K was found very weak in the windows and especially in our spectral region. This is consistent with the fact that our room temperature value and CAVIAR value at 402 K [16] agree within their 30 % error bars.

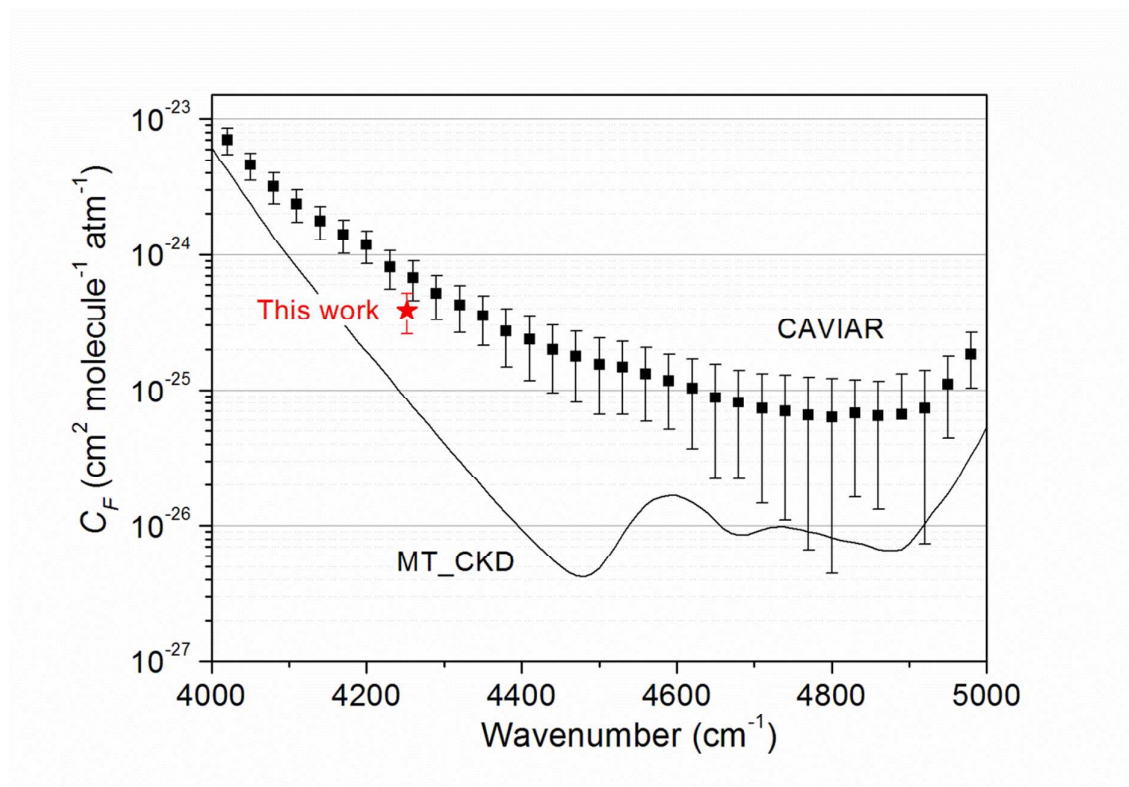


Figure 9. Spectral dependence of the foreign-continuum cross-section, C_F , derived from the MT_CKD V2.5 model [13] at 296 K (black solid line), measured in this work (red star) at room temperature and in Ref. [16] (black squares) at 402 K. Note the logarithmic scale adopted for the ordinate axis.

The room temperature contributions of the self- and foreign-absorptions of water in air at an air pressure of 1 atm are plotted in Figure 10 *versus* the water vapor partial pressure. In this plot, the absorption coefficients at 4250 cm^{-1} , calculated using the cross section values obtained in this work are compared to the corresponding CAVIAR [3,16] and MT_CKD values. For a partial pressure of water of 21 Torr at 296 K, the CAVIAR total (self plus foreign) continuum reaches a value of $16.4 \times 10^{-7} \text{ cm}^{-1}$ significantly larger than our and MT_CKD values of 9.1×10^{-7} and $5.3 \times 10^{-7} \text{ cm}^{-1}$, respectively. The main difference between our results and the MT_CKD model concerns the larger foreign continuum contribution which represents about one third of our total continuum but only 10% of the total MT_CKD continuum.

For a tropical atmosphere in clear sky conditions, our data lead to a much more limited additional absorption compared to that calculated in [16] using the CAVIAR continuum instead of the MT_CKD model. From Fig. 6 of Ref [16], it appears that the additional absorption is mainly due to the 2.1 μm window showing the need for low uncertainty measurements in that window and particularly in its center.

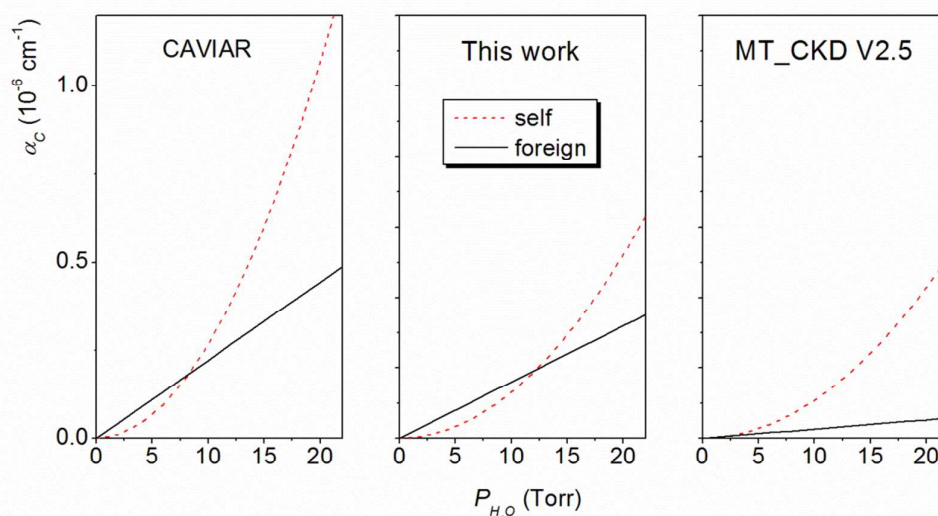


Figure 10. Self- (red dashed line) and foreign- (black solid line) water vapor continuum contributions calculated at 4250 cm^{-1} from the cross-sections reported in [3,16] (left panel), in this work (center panel) and in [13] (right panel). The different contributions are calculated versus the water vapor partial pressure and for a foreign pressure of 1 atm at room temperature.

5. Concluding remarks

A newly developed cavity ring down spectrometer has allowed for the first laser determination of the self- and foreign-cross-sections of water vapor at room temperature near 4250 cm^{-1} . The cross-section values were retrieved from a fit of the pressure dependence of the continuum absorption coefficients after subtraction of the local water monomer lines contribution calculated using HITRAN2012. As expected, the self- and foreign- absorption continua were found to vary quadratically with the water vapor pressure and linearly with the pressure of air added into the CRDS cell containing water vapor at a constant partial pressure, respectively. The derived C_F and C_S values are provided near 4250 cm^{-1} with error bar of 5 and 30 %, respectively.

The present work near 4250 cm^{-1} , together with our previous CRDS results at room temperature in the $1.6\text{ }\mu\text{m}$ window [18,19], are consistent with the MT_CKD 2.5 self-continuum values. This agreement provides a validation of this standard model widely used to implement the water continuum absorption in atmospheric radiative transfer codes. This validation is particularly convincing at the frequency of the present measurements where the self-continuum is stronger and where no effect of water adsorbed on the CRDS mirrors, as evidenced in the $1.6\text{ }\mu\text{m}$ window, were found. The performances of our CRDS set up allowed measuring a 7 % decrease of the C_S values over a 8 cm^{-1} spectral interval of our measurements providing a further test of the MT_CKD model which predicts a 9 % variation. In contrast, it seems to indicate that FTS measurements of Refs [3] and [17] overestimate the self-continuum cross-section at room temperature in the $2.3\text{ }\mu\text{m}$ window.

We nevertheless note an important difference for the foreign-continuum, our values being approximately 4.5 times higher than the MT_CKD V2.5 values. Such a disagreement largely exceeds our error bar which is estimated to be on the order of 30 % for the foreign continuum cross section. In addition, if we consider that there is almost no temperature dependence of the foreign continuum near 4250 cm^{-1} as observed in [16], our foreign-continuum value is compatible, within the error bars (about 30 %), with the CAVIAR value reported at 402 K.

In summary, around 4250 cm^{-1} , the observed differences between our self and foreign values and the FTS data are within the error bars. Nevertheless, we note that the self-continuum cross sections reported by FTS in Refs. [3] and [17] are mostly identical in the 2.2 , 1.6 and $1.25\text{ }\mu\text{m}$ windows ($C_S \approx 4 \times 10^{-23}\text{ cm}^2\text{ molecule}^{-1}\text{ atm}^{-1}$) and do not show significant frequency dependence over

each window. This almost constant C_s value corresponds to a 1 % shift of the baseline of the FTS spectrum when the long multipass cell is filled with 10 Torr of water. The FTS measurements of the foreign-continuum at high temperature of [16] are expected to be more accurate because the continuum optical depth and corresponding uncertainty were about 0.1 and 0.003, respectively. Even if the discrepancies between the FTS and CRDS measurements remain largely unexplained, we believe that the higher sensitivity of the CRDS technique and the small size of our CRDS set up (the CRDS cell has a volume of about 150 cm³) make our experimental approach more suitable than FTS for continua absorption measurements in the windows where small variations of the spectra baseline have to be detected.

In a near future, we plan to use new DFB laser diodes or VECSELs (Vertical External Cavity Surface Emitting Laser) to extend the spectral range accessible with our CRDS spectrometer and characterize the water continuum over the entire 2.1 μm transparency window. The region of higher transparency near 4700 cm⁻¹ where large discrepancies exist between MT_CKD, FTS and Bicknell's C_s values is particularly interesting. A further extension of the present study will consist in studying the temperature dependence of the water continuum which is of major interest for atmospheric applications.

Acknowledgements

This project is supported by the LabexOSUG@2020 (ANR10 LABX56) and the LEFE-ChAt program from CNRS-INSU. PC thanks CNRS for a three months support at LIPhy-Grenoble. This work was performed in the frame of the Laboratoire International Associé SAMIA between CNRS (France) and RFBR (Russia).

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