

The water vapor for eign-continuum in the 1.6 $\,\mu{\rm m}$ window by CRDS at room temperature

D. Mondelain, S. Vasilchenko, S. Kassi, A. Campargue

▶ To cite this version:

D. Mondelain, S. Vasilchenko, S. Kassi, A. Campargue. The water vapor for eign-continuum in the 1.6 $\mu \rm m$ window by CRDS at room temperature. Journal of Quantitative Spectroscopy and Radiative Transfer, 2020, 246, pp.106923. 10.1016/j.jqsrt.2020.106923 . hal-02935362

HAL Id: hal-02935362 https://hal.science/hal-02935362v1

Submitted on 17 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Manuscript Details

Manuscript number	JQSRT_2020_37
Title	The water vapor foreign-continuum in the 1.6 μm window by CRDS at room temperature
Article type	Full Length Article

Abstract

Water vapour foreign-continuum absorption cross-sections, CF, are measured for the first time at room temperature in the 1.6 µm transparency window, of importance for atmospheric applications. The measurements are performed by cavity ring down spectroscopy (CRDS) at 15 selected spectral data points. These data, covering the 5700-6640 cm-1 spectral range, are derived from the variation of the absorption signal during pressure ramps of humidified air up to 1 atm with a typical 1% humidity rate. The foreign-continuum absorption was obtained as the excess of the measured loss rate compared to the sum of the loss rate measured with dry air, the local water monomer contribution and the self-continuum absorption. CF values were derived from the linear dependence of the foreign-continuum absorption with the product of the partial pressures of water vapour and air. The semi-empirical MT_CKD CF values are found significantly underestimated in the centre of the window. The temperature dependence is discussed using high temperature measurements available in the literature.

Keywords	Water vapor; foreign-continuum; MT_CKD model; CRDS; transparency window; atmosphere	
Corresponding Author	Didier Mondelain	
Corresponding Author's Institution	LIPhy CNRS-UGA	
Order of Authors	Didier Mondelain, Semen Vasilchenko, Samir Kassi, alain Campargue	
Suggested reviewers	Eli Mlawer, manfred birk, Keith Shine	

Submission Files Included in this PDF

File Name [File Type]

- Cover Letter.docx [Cover Letter]
- highlights.docx [Highlights]
- graphical abstract.jpg [Graphical Abstract]
- Submitted_Version.pdf [Manuscript File]
- conflict of interest.docx [Conflict of Interest]
- Author statement.docx [Author Statement]

Submission Files Not Included in this PDF

File Name [File Type]

Supplementary_Material.txt [Supplementary Material]

To view all the submission files, including those not included in the PDF, click on the manuscript title on your EVISE Homepage, then click 'Download zip file'.

Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given: Data will be made available on request



Laboratoire Interdisciplinaire de Physique (ex Spectrométrie Physique)

www-liphy.ujf-grenoble.fr Unité Mixte de Recherche 5588 CNRS – Université Joseph Fourier Grenoble 1 BP 87 – 38402 ST MARTIN D'HERES Cedex France

Votre correspondant : D. Mondelain

tél. +33 4 76 51 43 29 fax. +33 4 76 63 54 95 Peter BERNATH

Editor in Chief JQSRT

St Martin d'Hères, the 21st of January 2020

Dear Sir,

Please find attached the version of our paper entitled: *The water vapor foreign-continuum in the 1.6 \mum window by CRDS at room temperature* by D. Mondelain, S. Vasilchenko, S. Kassi, A. Campargue, submitted to JQSRT.

Best regards Didier Mondelain

- First water vapour foreign-continuum measurements at 296 K in the 1.6 μm window
- CRDS loss rates were measured during pressure ramps of humidified air
- Cross-sections are provided for 15 spectral points between 5700 and 6750 cm⁻¹
- Derived foreign cross-sections are larger than the semi-empirical MT_CKD values



1	The water vapor foreign-continuum		
2	in the 1.6 µm window by CRDS at room temperature		
3			
4	D. Mondelain ^{1*} , S. Vasilchenko ^{1,2} , S. Kassi ¹ , A. Campargue ¹ ,		
$5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \\ 22 \\ 23 \\ 24 \\ 25 \\ 27 \\ 28 \\ 29 \\ 30 \\ 31 \\ 32 \\ 33 \\ 34 \\ 5 \\ 36 \\ 37 \\ 38 \\ 9 \\ 41 \\ 42 \\ 42 \\ 42 \\ 42 \\ 42 \\ 42 \\ 42$	¹ Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France ² Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of Science, 1 Akademician Zuev square, 634021 Tomsk, Russia *Corresponding author: Didier Mondelain (didier. mondelain@univ-grenoble-alpes.fr)		
44			
45 46	Kay words		
40			
47	water vapor; toreign-continuum; M1_CKD model; CRDS; transparency window, atmosphere		
48			

49 Abstract Water vapour foreign-continuum absorption cross-sections, C_F , are measured for the first time 50 at room temperature in the 1.6 µm transparency window, of importance for atmospheric 51 applications. The measurements are performed by cavity ring down spectroscopy (CRDS) at 52 15 selected spectral data points. These data, covering the 5700-6640 cm⁻¹ spectral range, are 53 derived from the variation of the absorption signal during pressure ramps of humidified air up 54 55 to 1 atm with a typical 1% humidity rate. The foreign-continuum absorption was obtained as the excess of the measured loss rate compared to the sum of the loss rate measured with dry 56 air, the local water monomer contribution and the self-continuum absorption. C_F values were 57 derived from the linear dependence of the foreign-continuum absorption with the product of 58 the partial pressures of water vapour and air. The semi-empirical MT CKD C_F values are 59 found significantly underestimated in the centre of the window. The temperature dependence 60 is discussed using high temperature measurements available in the literature 61 62

63 **1. Introduction**

Water vapour is known to strongly absorb the infrared radiations in the Earth's atmosphere 64 and thus to play a key role in its radiative budget [1]. In addition to the usual absorption by 65 water rovibrational lines, water vapour is responsible for an absorption slowly varying with 66 wavenumber, the so-called water vapour continuum. Paynter and Ramaswamy studied the 67 impact of this continuum in the atmospheric radiative transfer using their own empirical 68 continuum model (BPS continuum) [2] and the semi-empirical MT CKD model [3,4]. These 69 models exhibit differences which can be particularly important in the mid- and shortwave IR 70 regions leading to significant changes (up to 1 Wm⁻²) of the atmospheric absorption. It is thus 71 important to produce accurate experimental absorption cross-sections to test and validate 72 73 these empirical models, in particular in the transparency windows where the relative impact of the continuum is the largest. Since now one decade, large experimental efforts have been 74 75 performed to complete the pioneer works of Burch [5,6,7], using different techniques: Fourier transform spectroscopy (FTS) [8,9,10,11], cavity enhanced absorption spectroscopy (CEAS) 76 [12,13,14,15,16,17,18,19,20,21], calorimetric interferometry [22,23] and photo-acoustic 77 spectroscopy [24]. This is particularly true for the self-continuum absorption due to the 78 79 interaction between two water molecules. As a result, the latest version (3.2) of the MT CKD self-continuum has been recently constrained in the 4.0, 2.1, 1.6 and 1.25 µm windows [25], 80 taking into account most of the CEAS cross-sections of Refs. [16,17,18,19,21]. 81

In the case of the foreign-continuum arising from interactions between water molecules and 82 83 molecular oxygen and nitrogen, scarce experimental data are available [26], in particular at room temperature. This includes in-band continuum measurements in the 3500-4000 cm⁻¹ 84 spectral range by direct absorption spectroscopy [7] and between 1300 and 7500 cm⁻¹ by FTS 85 [27]. As concerned the transparency windows, cross-sections provided by FTS [28,29,30] in 86 the mid-IR windows and by cavity ring down spectroscopy (CRDS) in the 2.1 um window 87 [19] have led to a significant increase of the MT CKD foreign-continuum since the 2.8 88 version [25]. Note that FTS data were reported by the CAVIAR consortium at high 89 temperature (350-430 K) over the wide 1.1 - 5.0 µm spectral range thus including the 1.6 µm 90 window of present interest [31]. Additional measurements by CRDS are available at 10.6 µm 91 [13], in the 0.94 µm absorption band [32] and, very recently, in the 2.1 µm window by our 92 group [20]. This latter work compared with [31] at high temperature shows a weak positive 93 temperature dependence of the foreign continuum also reported in the infrared in the 296-363 94 K range [28,29] and in the 260-360 K range near 183 GHz [33]. 95

96 Note that these experimental investigations, in particular the temperature dependence, may 97 provide insights on the origin of the continuum which can be due to different processes like 98 the far wings of the rovibrational lines, water dimers (in the case of the self-continuum) and 99 collision-induced absorption (CIA) [34,35].

The present work is part of an extensive study that we conduct since several years to better 100 characterize the water vapour continuum absorption in the short-wave and mid-infrared 101 transparency windows [14,15,16,17,18,19,20,21]. The self-continuum including its 102 temperature dependence was investigated by CRDS in these references. Because of the 103 104 weakness of the signal to be measured, the experiment is particular challenging in the 1.6 μ m window. This applies in particular for the foreign-continuum measurements which require 105 106 relatively large changes in the gas pressure which may affect the optical alignment. In the 107 following part 2, we will present the experimental procedure adopted for the determination of 108 the foreign-continuum cross-sections at room temperature at 15 selected spectral points of the 1.6 µm window. Data acquisition by CRDS and data treatment as well as the error budget will 109 110 be discussed in part 3 and the resulting data will be compared to experimental data available in the literature and to the MT CKD model in part 4. 111

112 113

2. Experimental

114 *2.1 The CRDS setups*

Measurements were performed using two cavity ring down spectrometers. As described in 115 [36], a distributed feedback (DFB) laser diode (either from Eblana Photonics or NEL) is 116 coupled into a high finesse cavity fitted by two mirrors with highly reflective coatings. Our 117 two spectrometers used mirrors optimized for the 1500-1700 nm and the 1730-1840 nm 118 spectral regions The output mirror of the cavity is mounted on a piezoelectric transducer to 119 periodically change the cell length allowing covering one free spectral range (FSR) of the 120 121 cavity and thus achieving resonance between the laser light and one longitudinal mode of the cavity. After a build-up time necessary to fill the cavity with photons at resonance, the 122 injection of laser light is stopped thanks to an acousto-optic modulator and the purely 123 124 exponential decay time of photons leaking from the cavity (*i.e.* the ring down (RD) time, τ) is measured with a photodiode. The fitted RD time is directly related to the absorption 125 coefficient of the absorbing gas, $\alpha(v)$, through equation (1). 126

127

$$\alpha(v) = \frac{1}{c\tau(v)} \quad \frac{1}{c\tau_0(v)} \tag{1}$$

With *c* the speed of light, *v* the laser frequency and τ_0 the ring down time with the optical cavity empty or filled with a non-absorbing gas. To measure the laser frequency, a part of the laser light was directed via a fibre either to an optical interferometer-based wavelength meter (model 621-A IR from Bristol, $\pm 1.5 \times 10^{-3}$ cm⁻¹ accuracy or model WA-1650 from Burleigh, $\pm 1.1 \times 10^{-3}$ cm⁻¹ accuracy) or to a Fizeau wavelength meter (High Finesse WS-U-30 IR, 6.6×10^{-4} cm⁻¹ accuracy) depending on the selected data point and on the availability of the instrument.

A 1000 mbar pressure gauge (model 622AB from MKS instruments) was installed on the cavity to continuously measure the total pressure with an accuracy of 0.15% between 100 and 1000 mbar. A temperature sensor (TSic 501 from IST, ± 0.1 K accuracy) was fixed on the external wall of the cavity and enveloped by thermal insulation foam to continuously record the temperature.

140 *2.2. Data acquisition*

Foreign continuum cross-sections were determined for 15 spectral points between 5700 cm⁻¹ and 6640 cm⁻¹ (see **Table 1**). Each spectral point corresponds to the frequency of the radiation delivered by a distributed feedback (DFB) laser diode. Some measurements were repeated several times to check the repeatability The spectral points were selected because they are located in spectral intervals mostly free of absorption lines and thus correspond to weak local monomer contribution. The following procedure was adopted to derive the foreign crosssection value at each selected spectral point.

The high finesse cavity was first flushed with dry air (Alphagaz 2 from Air Liquide, purity > 148 99.9999%) at a total pressure of 700 Torr, regulated with a solenoid valve and a proportional 149 integral software based loop acting on the gas flow. A spectrum, including at least one 150 isolated water line reported in HITRAN2016 [37] with an accuracy between 1% and 2% 151 (called the reference line, hereafter), was recorded to check the low residual water vapour 152 concentration (typically on the order of 100 ppmv). The loss rate, $\frac{1}{c\tau_0(v)}$, at the laser frequency 153 fixed to one of the selected spectral points was measured during pressure ramp of dry air 154 155 decreasing from 700 Torr to 350 Torr (Figure 1). The typical duration of the pressure ramp was a few minutes. 156

As mentioned above a major difficulty of the experiment is that the amplitude of the pressure variation required to measure the foreign-continuum induces significant changes in the optical alignment of the CRDS cavity. As illustrated in the dry air recordings of **Fig. 1**, the pressure induced variation of the loss rate is mostly negligible on the edges of the window but, in the centre of the window, reaches values on the order of the additional losses due to water in the humidified air recordings. This would prevent foreign-continuum determination if the observed pressure induced variation were not repeatable. In fact, as illustrated in the superimposed traces of the dry air recordings presented in **Fig. 1**, the pressure effect on the optical alignment was checked to be highly repeatable allowing to use dry air pressure ramps as zero absorption baseline of the humidified air pressure ramps.

167 After the dry air recording, the cell was evacuated and filled with humidified air up to 700 Torr using a home-made humidifier [20]. Humidified air was flushed until a constant water 168 vapour concentration of typically 1% was achieved (Above this value, the water concentration 169 was not stable enough. In order to check the stability of the water partial pressure, a series of 170 consecutive CRDS spectra, including the reference water line, was recorded. For each 171 spectrum, the concentration was deduced from a fit to the water absorption line using a Voigt 172 profile. Once the water relative concentration in the cell was stabilized within better than 1% 173 (typically after 60 min), the injection of humidified air was stopped and the loss rates were 174 measured at the selected spectral point, during pressure ramp decreasing from 700 to 350 Torr 175 (Figure 1). An additional spectrum around the reference line was recorded at 350 Torr to 176 177 check that the water vapour concentration has remained unchanged during the ramp.

For this type of measurements, the stability of the ramp is essential. This is why we checked 178 179 carefully both the short-term and long-term stability of our set-up by recording several decreasing and increasing dry air ramps consecutively and comparing dry air ramps recorded 180 at several hours of distance and/or at different days for a given spectral point. We observed a 181 very good repeatability with no detectable changes on the short term scale (Figure 1) and 182 changes of 5×10^{-10} cm⁻¹ (offset) at maximum on the long term scale (over days) which 183 represents between 2% and 50% of the maximum measured absorption of the foreign-184 continuum, depending on the considered spectral point. Let us mention that pressure ramps 185 were restricted to the 350 - 700 Torr range as a small hysteresis, probably caused by changes 186 in the mirror alignment, was observed when the cell was fully evacuated. Note that the 187 procedure described here based on pressure ramps at fixed frequency was adopted because it 188 is less time consuming than that applied in reference [20], where spectra of air with different 189 190 water vapour concentrations were recorded.





Figure 1. Variation of the CRDS loss rate for humidified and dry air pressure ramps on the low energy edge (5752 cm^{-1}) and near the center (6022 cm^{-1}) of the 1.6 µm window. Note the variation of the loss rate of the dry air recordings with pressure due to a change of the mirrors alignment. This variation is checked to be repeatable by the superposed results obtained here for three dry air pressure ramps at 6022 cm⁻¹ (lower panel). Note the different amplitude of the losses due to water vapor (green) at 5752 cm⁻¹ and 6022 cm⁻¹

198 **3.** Analysis and resulting C_F cross-sections

199 3.2 Data analysis and C_F cross-sections retrieval

In a mixture of water vapor in air, the total absorption coefficient can be expressed as the sum of four terms:

 $\alpha_{tot}(\nu, T) = \alpha_{amity} + \alpha_{WMI} + \alpha_{WCS} + \alpha_{WCE}$

202

203

$$= \alpha_{cavity} + \alpha_{WML} + \frac{1}{kT}C_S(\nu, T)P_{H_20}^2 + \frac{1}{kT}C_F(\nu, T)P_{H_20}P_{air}$$
(2)

where α_{cavity} , α_{WML} , α_{WCS} and α_{WCF} are the contributions due to the cavity, water vapor "monomer local lines" (WML), water vapor self-continuum (WCS) and foreign-continuum (WCF), respectively. C_S and C_F cross-sections are expressed in cm²molecule⁻¹atm⁻¹.

From Equation (2), the foreign continuum absorption for a total pressure $P = P_{air} + P_{H_2O}$, is thus obtained by subtracting three contributions from the measured humidified air absorption (α_{tot}) : the dry air signal (α_{cavity}) for the same total pressure, *P*, corresponding to the losses of the cavity in absence of water vapor, the contribution of the air-broadened rovibrational lines, α_{WML} , and the water vapor self-continuum absorption at the P_{H_2O} partial pressure. Note that at a total pressure of 700 Torr, losses due to Rayleigh scattering in dry air and in air humidified with 1% water concentration differ by a negligible quantity of 2×10^{-11} cm⁻¹ calculated from [38].



215

Figure 2. Humidified air pressure ramp recorded at 5715.30 cm⁻¹ (left panel) and 6022.06 cm⁻¹ (right panel) after subtraction of the dry air ramp (black solid line). The water monomer local contribution (α_{WML}) , the self- (α_{WCS}) and the foreign-continuum contributions (α_{WCF}) are also plotted. The water relative concentration, P_{H_20}/P_{air} , on the order of 1% was maintained constant during the pressure ramp.

After subtraction of the baseline, the quantity α_{tot} $\alpha_{cavity} = \alpha_{WML} + \alpha_{WCS} + \alpha_{WCF}$ shows a linear dependence with $P_{H_20}P_{air}$ as illustrated in **Figure 2**. In particular, note the linearity of α_{tot} α_{cavity} achieved at 6022.1 cm⁻¹ confirming that the pressure effects on the mirror alignment, although important (see lower panel of **Figure 1**), is corrected by using the dry air measurements. The lines contribution was simulated at the selected spectral points, for total pressures of 350, 500, 600 and 700 Torr and the P_{H_20} partial pressure fixed to its measured value (corresponding to about 1% concentration). Simulations were performed using the

HITRAN2016 line list [37], using a Voigt profile and the standard [-25 cm⁻¹, +25 cm⁻¹] 228 convention cut-off for the line wings [9]. The selected spectral points, v_i , being located at 229 frequency values far from line centers, the pressure dependence of α_{WML} is proportional to 230 $P_{H_2O}P_{air}$. The pressure dependence of the simulated α_{WML} values were thus fitted with a 231 second order polynomial which was used to subtract the local line contribution over the 232 pressure ramp (Figure 2). The self-continuum contribution was calculated using the self-233 234 continuum cross-sections from [20]. As the pressure ramps were performed at constant humidity rate $(P_{H_2O}/P_{air} \approx 1\%)$, α_{WCS} is also proportional to $P_{H_2O}P_{air}$. The relative 235 236 contributions of the local monomer and of the self- and foreign-continuum, to the total absorption are provided in Table 1. 237

Figure 3 shows the achieved linear dependence of α_{WCF} versus $P_{H_20}P_{airr}$ for different selected spectral points. The change of the slope illustrates the frequency dependence of the foreign-continuum cross-sections which were derived from a linear fit (Eq.2). A small positive offset is observed at null pressure. The origin of this offset is not clear. After several tests, we only observed that the slope seems not being affected by a change of the offset value. No offset of this sort was observed in our previous measurements in the 2.3 µm window [20].



245

Figure 3. Absorption coefficient of the foreign-continuum for pressure ramps obtained for different
selected spectral points. Two linear fit are also added to show the small observed offsets.

The C_F values derived from the procedure described above are listed in **Table 1** and presented in **Figure 4**. A 5th order polynomial fit of the C_F cross-sections (weighted by their uncertainties) is also shown in **Figure 4** and was used to provide C_F cross-sections every 10 cm⁻¹ between 5700 cm⁻¹ and 6640 cm⁻¹ as Supplementary Material.

Table 1. Foreign-continuum cross-sections in the 1.6 μ m window and their 1 σ estimated uncertainties in units of the last digit (in parenthesis). The relative contributions of the "local line monomer", selfand foreign continuum to the total absorption are also given in the three last columns. During the whole period of measurements temperature varied between 296 K and 298.5 K.

256

ν	C_F	$\alpha_{WML}/\alpha_{tot}$	$\alpha_{WCS}/\alpha_{tot}$	$\alpha_{WCF}/\alpha_{tot}$
cm ⁻¹	cm ² molecule ⁻¹ atm ⁻¹	%	%	%
5702.13	$1.12(11) \times 10^{-25}$	48.5	17.9	33.6
5715.30	$1.07(16) \times 10^{-25}$	49.1	17.3	33.6
5752.04	2.88(95)×10 ⁻²⁶	61.0	21.3	17.7
5816.60	2.60(28)×10 ⁻²⁶	29.4	37.3	33.3
5842.20 $1.61(30) \times 10^{-26}$		28.8	39.7	31.5
	1.90(30)×10 ⁻²⁶			
	2.20(30)×10 ⁻²⁶			
5875.20	2.42(24)×10 ⁻²⁶	30.5	29.3	40.2
	2.33(24)×10 ⁻²⁶			
5905.72	$1.33(20) \times 10^{-26}$	25.5	37.1	37.4
	$1.76(20) \times 10^{-26}$			
	1.53(20)×10 ⁻²⁶			
5933.75	$1.03(10) \times 10^{-26}$	21.3	41.5	37.2
	$1.21(10) \times 10^{-26}$			
	$1.14(10) \times 10^{-26}$			
	1.17(10)×10 ⁻²⁶			
	$1.17(10) \times 10^{-26}$			
	$1.15(10) \times 10^{-26}$			
	$1.18(10) \times 10^{-26}$			
6022.06	7.4(15)×10 ⁻²⁷	25.9	30.6	43.5
6120.45	7.0(12)×10 ⁻²⁷	14.6	34.0	51.4
6224.09	3.5(12)×10 ⁻²⁷	17.9	36.6	45.5
6369.00 ^a	<5×10 ⁻²⁷			
6511.97	$6.9(65) \times 10^{-27}$	85.4	5.9	8.7
6562.18	9.1(40)×10 ⁻²⁷	79.4	8.0	12.6
6637.62	4.7(14)×10 ⁻²⁶	71.8	6.9	21.3

257

^a Due to the large estimated uncertainty, only an upper limit value can be given at 6369 cm⁻¹.





Figure 4. Overview of the foreign-continuum cross-sections, C_F , in the 1.6 μ m window obtained in this work and found in the literature. The red solid line corresponds to the fit of our data with a 5th order polynomial. Note that for comparison purposes, the C_F values are density normalized and are given in cm^2 molecule⁻¹.

264 *3.3 Error budget*

Uncertainties on the derived C_F values have been calculated with the error propagation approach using Eq. 2 and assuming uncorrelated variables. As discussed earlier, the baseline stability was evaluated to be below 5×10^{-10} cm⁻¹. Temperature and total pressure are measured with accuracies of 0.1K and 0.15%, respectively. Their contributions are almost negligible. The uncertainties on C_S values used here are reported in [20].

The knowledge on the water vapour partial pressure is the main contributor to the error budget through the monomer contribution which is proportional to P_{H_2O} and the self-continuum contribution proportional to $P_{H_2O}^2$. The partial pressure is derived from the fitted area of wellisolated H₂O lines with intensities reported in HITRAN2016 with uncertainties better than 2% [37]. This value is adopted as the uncertainty on P_{H_2O} considering that the quality figure of the

- fits, defined as the ratio between peak signal and *rms* fit residuals, of several hundred, limitsthe error on the fitted area below 1%.
- The monomer contribution uncertainties were determined by taking into account the error bars on the line intensities, self-broadening, air-broadening coefficients and water vapour pressure. Four simulations, $\delta_i(v)$, were performed, each of them with either, the intensities,

280 γ_{self} , γ_{air} coefficients or P_{H_2O} values increased by their error bar. The uncertainty on α_{WML} was 281 obtained from: $\delta \alpha_{WML}(\nu) = [\sum_{i=1}^{4} \delta_i(\nu)^2]^{1/2}$.

The uncertainties detailed above are of type-B. To quantify statistical (type-A) uncertainties 282 we recorded consecutively six decreasing pressure ramps of humidified air at the selected 283 spectral point of 5933.75 cm⁻¹ chosen because of a limited impact of the uncertainty on P_{H_2O} . 284 Between each ramp, the cell was filled again with humidified air from 350 Torr to 700 Torr 285 and two CRDS spectra were recorded to check the stability of the water concentration and 286 determine this concentration. All the ramps were base line corrected using the same dry air 287 ramp recorded just before. Nevertheless, a dry air ramp recorded just after exactly superposed 288 to the ramp used. A relative standard deviation of 2.1% was obtained on the derived C_F values 289 showing the very good short term repeatability. Two months before a C_F value 13% lower 290 than the averaged value on the 6 ramps was measured for the same spectral point with the 291 other CRDS spectrometer used in this work showing that largest statistical uncertainties have 292 to be considered. We also achieved measurements at 5842.24 cm⁻¹, 5905.72 cm⁻¹ and 6369.00 293 cm⁻¹ done each time at three different days. From these data we extended to each spectral 294 point a statistical uncertainty that we chosen inversely proportional to the ratio between the 295 value of α_{WCF} at 0.08 atm² (i.e. the maximum of the pressure ramps) and the minimum 296 297 detectable absorption coefficient α_{min} for the pressure ramp.

Combining the type-A and type-B uncertainties, we obtained the final uncertainties reportedin Table 1 for each spectral point.

- 300
- 301

4 Comparison to literature data

To our knowledge, the only previous determinations of foreign-continuum cross-sections 302 available in the 1.6 µm window have been reported in [31] by the CAVIAR consortium at 303 304 high temperature. In this work, C_F values were derived from spectra recorded at a single pressure value, with a Fourier transform spectrometer coupled to a White cell providing a 305 17.7 m optical path length. To increase the absorption continuum signal, the cell was heated 306 between 350 K and 430 K allowing for water vapour partial pressure to be increased up to 266 307 mbar and 600 mbar, depending on the cell temperature. No temperature dependence of the 308 foreign-continuum could be evidenced in the 350-430 K temperature interval of the FTS 309 measurements. The spectrally smoothed CAVIAR C_F values reported at 400 K [31] are 310 plotted in Figure 4 with their corresponding error bars ranging between about 25% and 120% 311 on the edges and near the centre of the window, respectively. Overall, the CAVIAR C_F values 312

(density normalized) at 400 K are larger than our cross-sections by factors between \sim 3 and \sim 8, 313 on the edges and near the centre of the window, respectively. Such important increase 314 between 296 K and 400 K is significantly larger than the FTS error bars [31] (see Figure 4). 315 Nevertheless, the fact that no clear temperature dependence was evidenced between the 316 317 CAVIAR measurements at 350 K and 430 K questioned the correctness and amplitude of the positive temperature dependence between 296 K and 400 K. Note that in the 2.3 µm window 318 [20], a constant C_F ratio of ~3 was observed over most of the window between the CAVIAR 319 and CRDS cross-sections (density normalized). Again, the significance of this variation close 320 to the 1σ error bar of the FTS C_F values, remains to be confirmed. 321

Finally, let us recall that the foreign-continuum temperature dependence in the windows is by no means similar to that of the self-continuum which exhibits a clear negative temperature dependence (see for example [9,17]).

Foreign-continuum provided by the latest version of the MT CKD model (MT CKD3.2) is 325 included in Figure 4 for comparison purposes. No temperature dependence is provided for the 326 MT CKD foreign cross-sections. For the low energy edge of the window, the MT CKD C_F 327 values are significantly larger than our measurements in contrast with the values in the centre 328 of the window which are smaller by a factor of ~9. Nevertheless, near the centre of the 329 330 window, the foreign continuum is very weak and the experimental uncertainty reaches almost 100%. More accurate measurements are thus required to be conclusive in the very centre of 331 the window, near 6300 cm^{-1} . 332

Finally, let us consider the humidified measurements by calorimetric interferometry reported 333 334 by Bicknell [22]. In the 2.3 µm window where the continuum is larger, we could calculate the self-contribution to Bicknell's continuum using our determination of the C_F values and 335 obtained a good agreement with our C_S value [20]. In the considered 1.6 μ m window, 336 Bicknell reported a total (self+foreign) continuum absorption coefficient of 3.2×10^{-8} cm⁻¹ at 337 6150 cm⁻¹ for a mixture of 18.75 Torr of H₂O in N₂ with a total pressure of 760 Torr (see [10] 338 for details). For the same experimental conditions, we calculate an absorption coefficient of 339 ~1×10⁻⁸ cm⁻¹ when using our present C_F determination of 5.4(9)×10⁻²⁷ cm² molec⁻¹ atm⁻¹ and 340 a C_8 value of 4.9(7)×10⁻²⁵ cm² molec⁻¹ atm⁻¹ from Ref. [20]. This difference by a factor of 3 is 341 outside the combined error bars and difficult to interpret on the basis of the scarce 342 experimental information provided in Ref.[22] (see [39] for discussion). Note that our C_F 343 determinations rely on careful study of the pressure dependence of the continuum signal while 344 Bicknell's measurements were performed at a single pressure [22]. 345

5. Conclusion

Water vapor foreign-continuum cross-sections have been obtained at room temperature in the 1.6 μ m window. The corresponding small cross-sections were derived from CRDS measurements during pressure ramps recorded at fixed spectral points between 5700 cm⁻¹ and 6640 cm⁻¹. Fifteen spectral points were selected to sample the window at frequencies corresponding to small contribution of the water monomer lines. The CAVIAR measurements at high temperature in the same window are larger in amplitude but show a similar wavelength dependence.

The foreign-continuum absorption is very weak at room temperature, in particular, in the very centre of the window. For instance, the absorption coefficient to be measured is on the order of 10^{-9} cm⁻¹ for 1 atm of humidified air with 1 % of water vapor (\approx 7 Torr). Measurements in this central region were made possible thanks to the very good repeatability of the loss rates of our CRDS set up. Although the dry air CRDS loss rates were found to be sensitive to the pressure variation during the pressure ramp, their dependence was found highly repeatable allowing us to use dry air recordings as baseline of the humidified air recordings.

- Two factors could help to decrease the C_F relative uncertainties which range between 10% 361 362 and 100%. Firstly, our home-made humidifier provides humidified air with stable water vapor relative concentration limited to 1% at most, corresponding to a relative humidity of 33% at 363 296 K. The increase by a factor of two of the water vapor partial pressure could help to 364 decrease the relative uncertainties. Secondly, the uncertainty on the water vapor partial 365 366 pressure (or concentration) is the main contributor to the final uncertainties through the selfcontinuum and the water monomer subtracted contributions. At the moment, a 2% uncertainty 367 is achieved on the knowledge of the water concentration in the used humidified air, mainly 368 due to the uncertainty on the intensity reported in HITRAN2016 for the water reference line 369 370 used to derive the water partial pressure. Alternative techniques as dew point mirror hygrometers are considered to improve the determination of the water vapor partial pressure 371 by at least a factor of two and thus the accuracy of the reported C_F values, in particular near 372 the centre of the window. 373
- 374

375 Acknowledgments

This project is supported by the Labex OSUG@2020 (ANR10 LABX56) and the LEFE-ChAt

377 program from CNRS-INSU.

378 References

[1] Cubasch U, Wuebbles D, Chen D, Facchini MC, Frame D, Mahowald N, Winther J-G, 2013: Introduction. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[2] Paynter D and Ramaswamy V, Variations in water vapor continuum radiative transfer with atmospheric conditions. J Geophys Res 2012;117:D16310. doi:10.1029/2012JD017504

[3] Clough SA, Kneizys FX, Davies RW. Line shape and the water vapor continuum. Atm Res 1989;23:229-241. doi:10.1016/0169-8095(89)90020-3

[4] Mlawer EJ, Payne VH, Moncet J, Delamere JS, Alvarado MJ, Tobin DC. Development and recent evaluation of the MT_CKD model of continuum absorption. Phil Trans R Soc A 2012;370:2520–2556. doi:10.1098/rsta.2011.0295

[5] Burch DE. Continuum absorption by H₂O. Report AFGL-TR-81-0300, Air Force Geophys. Laboratory, Hanscom AFB, MA, 1982.

[6] Burch DE, Alt RL. Continuum absorption by H_2O in the 700 – 1200 cm⁻¹ and 2400 – 2800 cm⁻¹ windows. Report AFGL-TR-84-0128, Air Force Geophys. Laboratory, Hanscom AFB, MA, 1984.

[7] Burch DE. Absorption by H_2O in narrow windows between 3000 and 4200 cm⁻¹. Report AFGL-TR-85-0036, Air Force Geophys. Laboratory, Hanscom AFB, MA, 1985.

[8] Paynter DJ, Ptashnik IV, Shine KP, Smith KM, McPheat R, Williams RG. Laboratory measurements of the water vapor continuum in the 1200–8000 cm⁻¹ region between 293 K and 351 K. J Geophys Res 2009;114:D21301. doi:10.1029/2008JD011355

[9] Ptashnik IV, McPheat RA, Shine KP, Smith KM, Williams RG. Water vapor self-continuum absorption in near-infrared windows derived from laboratory measurements. J Geophys Res 2011;116: D16305. doi:10.1029/2011JD015603

[10] Ptashnik IV, Petrova TM, Ponomarev YN, Shine KP, Solodov AA, Solodov AM. Near-infrared water vapour self-continuum at close to room temperature. J Quant Spectrosc Radiat Transfer 2013;120:23–35. doi:10.1016/j.jgsrt.2013.02.016

[11] Ptashnik IV, Petrova TM, Ponomarev YN, Solodov AA, Solodov AM. Water vapor continuum absorption in near-IR atmospheric windows. Atmos Oceanic Opt 2015;28:115–120. doi:10.1134/S102485601502009

[12] Cormier JG, Ciurylo R, Drummond JR. Cavity ringdown spectroscopy measurements of the infrared water vapor continuum. J Chem Phys 2002;116:1030–1034. doi:10.1063/1.1425825

[13] Cormier JG, Hodges JT, Drummond JR. Infrared water vapor continuum absorption at atmospheric temperatures. J Chem Phys 2005;122:114309. doi: 10.1063/1.1862623

[14] Mondelain D, Aradj A, Kassi S, Campargue A. The water vapour self-continuum by CRDS at room temperature in the 1.6 μ m transparency window. J Quant Spectrosc Radiat Transfer 2013;130:381–91. doi: 10.1016/j.jqsrt.2013.07.006.

[15] Mondelain D, Manigand S, Manigand S, Kassi S, Campargue A. Temperature de- pendence of the water vapor self-continuum by cavity ring-down spectroscopy in the 1.6 µm transparency window. J Geophys Res Atmos 2014;119(9):2169–8996. doi: 10.1002/2013JD021319.

[16] Campargue A, Kassi S, Mondelain D, Vasilchenko S, Romanini D. Accurate laboratory determination of the near infrared water vapor self-continuum: A test of the MT_CKD model. J Geophys Res Atmos 2016;121:13,180 – 13,203. doi:10.1002/2016JD025531

[17] Richard L, Vasilchenko S, Mondelain D, Ventrillard I, Romanini D, Campargue A. Water vapor self-continuum absorption measurements in the 4.0 and 2.1 µm transparency windows. J Quant Spectrosc Radiat Transf 2017;201:171–179. doi: 10.1016/j.jqsrt.2017.06.037

[18] Lechevallier L, Vasilchenko S, Grilli R, Mondelain D, Romanini D, Campargue A. The water vapour self-continuum absorption in the infrared atmospheric windows: new laser measurements near 3.3 and 2.0 µm. Atmos Meas Tech 2018;11:2159–2171. doi:10.5194/amt-11-2159-2018

[19] Mondelain D, Vasilchenko S, Ĉermák P, Kassi S, Campargue A. The self- and foreign-absorption continua of water vapor by cavity ring-down spectroscopy near 2.35 μm. Phys Chem Chem Phys 2015;17:17,762–17,770. doi: 10.1039/c5cp01238d

[20] Vasilchenko S, Campargue A, Kassi S, Mondelain D, The water vapour self- and foreigncontinua in the 1.6 μm and 2.3 μm windows by CRDS at room temperature. J Quant Spectrosc Radiat Transfer 2019;227:230–238. doi: 10.1016/j.jqsrt.2019.02.01

[21] Ventrillard I, Romanini D, Mondelain D, Campargue A. Accurate measurements and temperature dependence of the water vapor self-continuum absorption in the 2.1 µm atmospheric window. J Chem Phys 2015;143:134304. doi: 10.1063/1.4931811]

[22] Bicknell WE, Cecca SD, Griffin MK. Search for low-absorption regions in the 1.6- and 2.1-µm atmospheric windows. J Directed Energy 2006;2:151–61.

[23] Fulghum SF, Tilleman MM. Interferometric calorimeter for the measurement of water-vapor absorption. J Opt Soc Am B – Opt Phys 1991;8:2401–2413. Doi:10.1364/josab.8.002401.

[24] Kapitanov VA, Osipov KY, Ptashnik IV. Photoacoustic measurements of the water vapor continuum absorption in the 1.6 μ m window. Optika Atmosfery i Okeana 2018;31:995–1000 [in Russian].

[25] http://rtweb.aer.com/continuum description.html

[26] Hartmann J-M,Tran H, Armante R, Boulet C, Campargue A, Forget F, Gianfrani L, Gordon I, Guerlet S, Gustafsson M, Hodges JT, Kassi S, Lisak D, Thibault F, Toon GC. Recent advances in collisional effects on spectra of molecular gases and their practical consequences, J Quant Spectrosc Radiat Transfer 2018;213:178–227. doi: 10.1016/j.jqsrt.2018.03.016

[27] Paynter D J, Ptashnik I V, Shine K P, Smith K M, McPheat R, Williams R G 2009 Laboratory measurements of the water vapour continuum in the 1200–8000 cm⁻¹ region between 293K and 351 K. J Geophys Res 114, D21301. doi:10.1029/2008JD011355

[28] Baranov YI. The continuum absorption in H_2O+N_2 mixtures in the 2000–3250 cm⁻¹ spectral region at temperatures from 326 to 363 K. J Quant Spectrosc Radiat Transfer 2011;112:2281–2286. doi:10.1016/j.jqsrt.2011.06.005

[29] Baranov YI, Buryak IA, Lokshtanov SE, Lukyanchenko VA, Vigasin AA. H_2O N_2 collisioninduced absorption band intensity in the region of the N_2 fundamental: ab initio investigation of its temperature dependence and comparison with laboratory data. Phil Trans R Soc A 2012;370:2691– 2709. doi: 10.1098/rsta.2011.0189.

[30] Baranov YI and LaffertyWJ. The water vapour self- and water-nitrogen continuum absorption in the 1000 and 2500 cm⁻¹ atmospheric windows. Phil Trans R Soc A 2012;370:2578–2589. doi: 10.1098/rsta.2011.0234

[31] Ptashnik IV, McPheat RA, Shine KP, Smith KM, Williams RG. Water vapour foreign-continuum absorption in near-infrared windows from laboratory measurements. Phil Trans R Soc A 2012;370: 2557–2577. doi:10.1098/rsta.2011.0218

[32] Reichert L, Andrés Hernández MD, Burrows JP, Tikhomirov AB, Firsov KM, Ptashnik IV. First CRDS-measurements of water vapour continuum in the 940 nm absorption band. J Quant Spectrosc Radiat Transf 2007;105:303–11. doi:10.1016/j.jqsrt.2006.10.010

[33] Brogniez H, English S, Mahfouf JF, Behrendt A, Berg W, Boukabara S, Buehler SA, Chambon P, Gambacorta A, Geer A, Ingram W, Kursinski ER, Matricardi M, Odintsova TA, Payne VH, Thorne PW, Tretyakov MY, Wang J. A review of sources of systematic errors and uncertainties in observations and simulations at 183 GHz. Atmos Meas Tech 2016;9:2207–2221. doi:10.5194/amt-9-2207-2016

[34] Serov EA, Odintsova TA, Tretyakov MY, Semenov ME. On the origin of the water vapour continuum absorption within rotational and fundamental vibrational bands. J Quant Spectrosc Radiat Transfer 2017;193:1–12. doi: 10.1016/j.jqsrt.2017.02.011

[35] Shine KP, Ptashnik IV, Rädel G. The Water Vapour Continuum: Brief History and Recent Developments, Surv Geophys 2012;33:535–555. doi:10.1007/s10712-011-9170-y

[36] Kassi S, Campargue A. Cavity ring down spectroscopy with 5×10^{-13} cm⁻¹ sensitivity. J Chem Phys 2012;137:234201. doi: 10.1063/1.4769974.

[37] Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, Birk M, Boudon V, Campargue A, Chance KV, Drouin BJ, Flaud JM, Gamache RR, Hodges JT, Jacquemart D, Perevalov, VI, Perrin A, Shine KP, Smith MAH, Tennyson J, Toon GC, Tran H, Tyuterev VG, Barbe A, Császár, AG, Devi VM, Furtenbacher T, Harrison JJ, Hartmann J-M, Jolly A, Johnson TJ, Karman T, Kleiner, I, Kyuberis AA, Loos J, Lyulin OM, Massie ST, Mikhailenko SN, Moazzen-Ahmadi N, Müller HSP,

Naumenko OV, Nikitin AV, Polyansky OL, Rey M, Rotger M, Sharpe SW, Sung K, Starikova E, Tashkun SA, Vander Auwera J, Wagner G, Wilzewski J, Wcisło P, Yu S, Zak EJ. The HITRAN2016 Molecular Spectroscopic Database. J Quant Spectrosc Radiat Transf 2017;203:3-69. doi: 10.1016/j.jgsrt.2017.06.038

[38] Thalman R, Zarzana K, Tolbert MA and Volkamer R. Rayleigh scattering cross-section measurements of nitrogen, argon, oxygen and air. J Quant Spectrosc Radiat Transfer 2014;147:171–177. doi: 10.1016/j.jqsrt.2014.05.030

[39] Shine KP, Campargue A, Mondelain D, McPheat RA, Ptashnik IV, Weidmann D. The water vapour continuum in near-infrared windows – Current understanding and prospects for its inclusion in spectroscopic databases. J Molec Spec 2016;327:193–208. doi: 10.1016/j.jms.2016.04.011

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

D. Mondelain : CRDS recordings, Data analysis, Writing the paper, S. Vasilchenko:
 Installation and test of the CRDS setup, S. Kassi: Software for data treatment and analysis,
 A. Campargue: Data analysis, Writing the paper