



HAL
open science

The water vapor foreign-continuum in the 1.6 μm 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 foreign-continuum in the 1.6 μm 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-02935362>

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

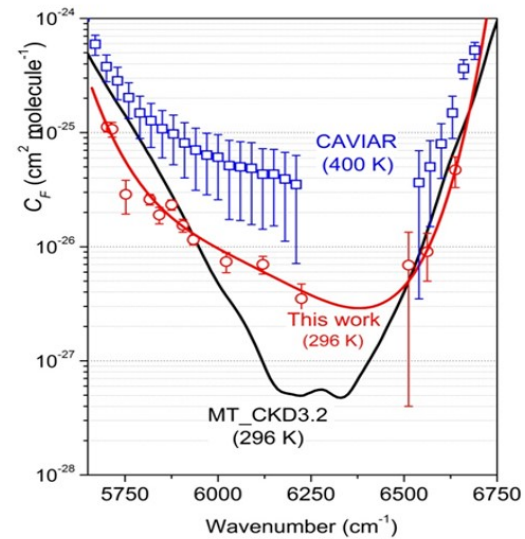
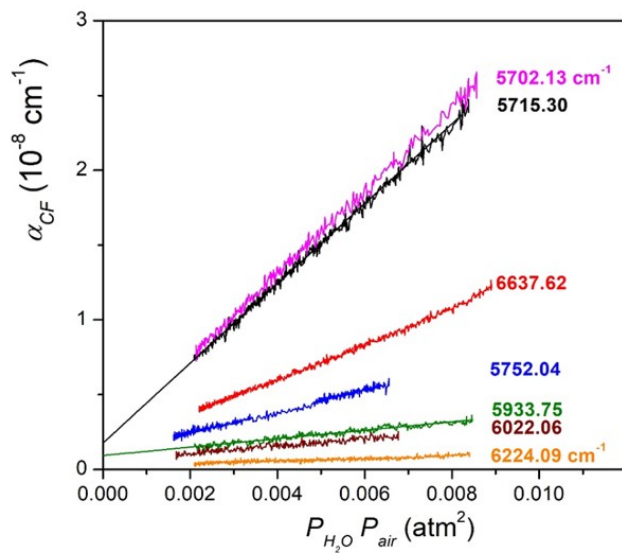
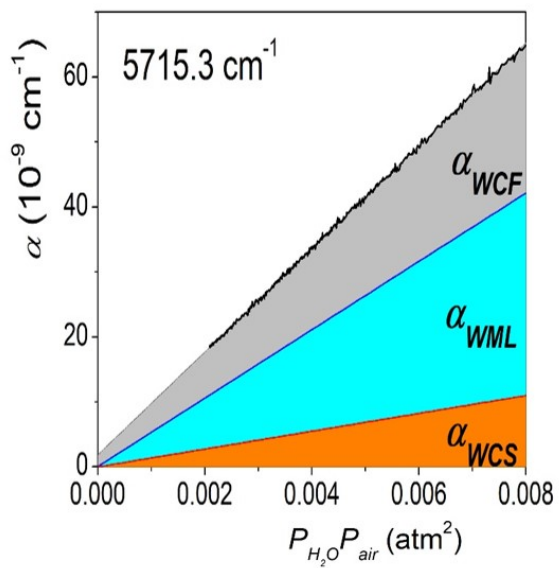
St Martin d'Hères, the 21st of January 2020

Dear Sir,

Please find attached the version of our paper entitled: *The water vapor foreign-continuum in the 1.6 μm 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. Kassi¹, A. Campargue¹,

5 ¹Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France

6 ²Laboratory of Molecular Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, SB, Russian Academy of
7 Science, 1 Akademician Zuev square, 634021 Tomsk, Russia
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 **Corresponding author: Didier Mondelain (didier.mondelain@univ-grenoble-alpes.fr)*
42
43
44
45

46 **Key words**

47 Water vapor; foreign-continuum; MT_CKD model; CRDS; transparency window, atmosphere
48

49
50
51
52
53
54
55
56
57
58
59
60
61
62

Abstract

Water vapour foreign-continuum absorption cross-sections, C_F , 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. C_F 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 C_F values are found significantly underestimated in the centre of the window. The temperature dependence is discussed using high temperature measurements available in the literature

63 1. Introduction

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

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

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].

100 The present work is part of an extensive study that we conduct since several years to better
101 characterize the water vapour continuum absorption in the short-wave and mid-infrared
102 transparency windows [14,15,16,17,18,19,20,21]. The self-continuum including its
103 temperature dependence was investigated by CRDS in these references. Because of the
104 weakness of the signal to be measured, the experiment is particular challenging in the 1.6 μm
105 window. This applies in particular for the foreign-continuum measurements which require
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
109 1.6 μm window. Data acquisition by CRDS and data treatment as well as the error budget will
110 be discussed in part 3 and the resulting data will be compared to experimental data available
111 in the literature and to the MT_CKD model in part 4.

112 **2. Experimental**

113 *2.1 The CRDS setups*

114 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 cavity and thus achieving resonance between the laser light and one longitudinal mode of the
121 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 exponential decay time of photons leaking from the cavity (*i.e.* the ring down (RD) time, τ) is
124 measured with a photodiode. The fitted RD time is directly related to the absorption
125 coefficient of the absorbing gas, $\alpha(\nu)$, through equation (1).
126

$$127 \quad \alpha(\nu) = \frac{1}{c\tau(\nu)} - \frac{1}{c\tau_0(\nu)} \quad (1)$$

128 With c the speed of light, ν the laser frequency and τ_0 the ring down time with the optical
129 cavity empty or filled with a non-absorbing gas.

130 To measure the laser frequency, a part of the laser light was directed via a fibre either to an
131 optical interferometer-based wavelength meter (model 621-A IR from Bristol, $\pm 1.5 \times 10^{-3} \text{ cm}^{-1}$
132 accuracy or model WA-1650 from Burleigh, $\pm 1.1 \times 10^{-3} \text{ cm}^{-1}$ accuracy) or to a Fizeau
133 wavelength meter (High Finesse WS-U-30 IR, $6.6 \times 10^{-4} \text{ cm}^{-1}$ accuracy) depending on the
134 selected data point and on the availability of the instrument.

135 A 1000 mbar pressure gauge (model 622AB from MKS instruments) was installed on the
136 cavity to continuously measure the total pressure with an accuracy of 0.15% between 100 and
137 1000 mbar. A temperature sensor (TSic 501 from IST, $\pm 0.1 \text{ K}$ accuracy) was fixed on the
138 external wall of the cavity and enveloped by thermal insulation foam to continuously record
139 the temperature.

140 *2.2. Data acquisition*

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

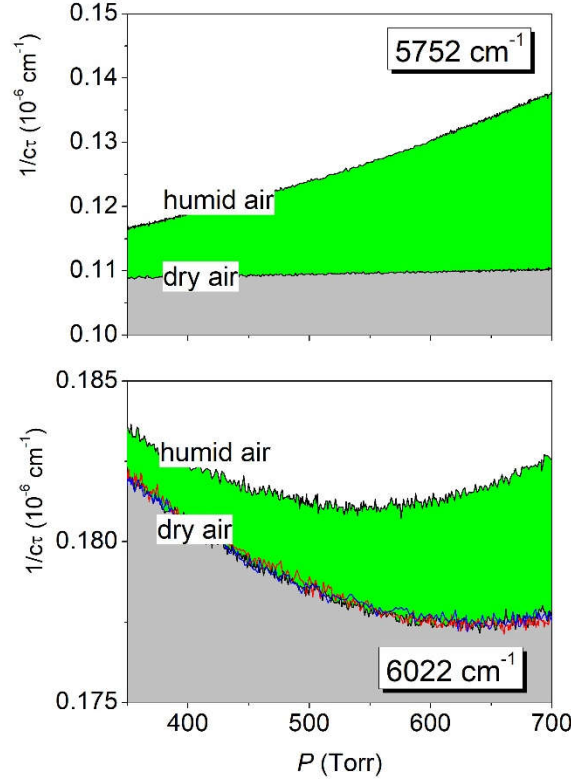
148 The high finesse cavity was first flushed with dry air (Alphagaz 2 from Air Liquide, purity $>$
149 99.9999%) at a total pressure of 700 Torr, regulated with a solenoid valve and a proportional
150 integral software based loop acting on the gas flow. A spectrum, including at least one
151 isolated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

157 As mentioned above a major difficulty of the experiment is that the amplitude of the pressure
158 variation required to measure the foreign-continuum induces significant changes in the optical
159 alignment of the CRDS cavity. As illustrated in the dry air recordings of **Fig. 1**, the pressure
160 induced variation of the loss rate is mostly negligible on the edges of the window but, in the
161 centre of the window, reaches values on the order of the additional losses due to water in the
162 humidified air recordings. This would prevent foreign-continuum determination if the

163 observed pressure induced variation were not repeatable. In fact, as illustrated in the
164 superimposed traces of the dry air recordings presented in **Fig. 1**, the pressure effect on the
165 optical alignment was checked to be highly repeatable allowing to use dry air pressure ramps
166 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
168 Torr using a home-made humidifier [20]. Humidified air was flushed until a constant water
169 vapour concentration of typically 1% was achieved (Above this value, the water concentration
170 was not stable enough. In order to check the stability of the water partial pressure, a series of
171 consecutive CRDS spectra, including the reference water line, was recorded. For each
172 spectrum, the concentration was deduced from a fit to the water absorption line using a Voigt
173 profile. Once the water relative concentration in the cell was stabilized within better than 1%
174 (typically after 60 min), the injection of humidified air was stopped and the loss rates were
175 measured at the selected spectral point, during pressure ramp decreasing from 700 to 350 Torr
176 (**Figure 1**). An additional spectrum around the reference line was recorded at 350 Torr to
177 check that the water vapour concentration has remained unchanged during the ramp.

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



191

192 *Figure 1. Variation of the CRDS loss rate for humidified and dry air pressure ramps on the low*
 193 *energy edge (5752 cm⁻¹) and near the center (6022 cm⁻¹) of the 1.6 μm window. Note the variation of*
 194 *the loss rate of the dry air recordings with pressure due to a change of the mirrors alignment. This*
 195 *variation is checked to be repeatable by the superposed results obtained here for three dry air*
 196 *pressure ramps at 6022 cm⁻¹ (lower panel). Note the different amplitude of the losses due to water*
 197 *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

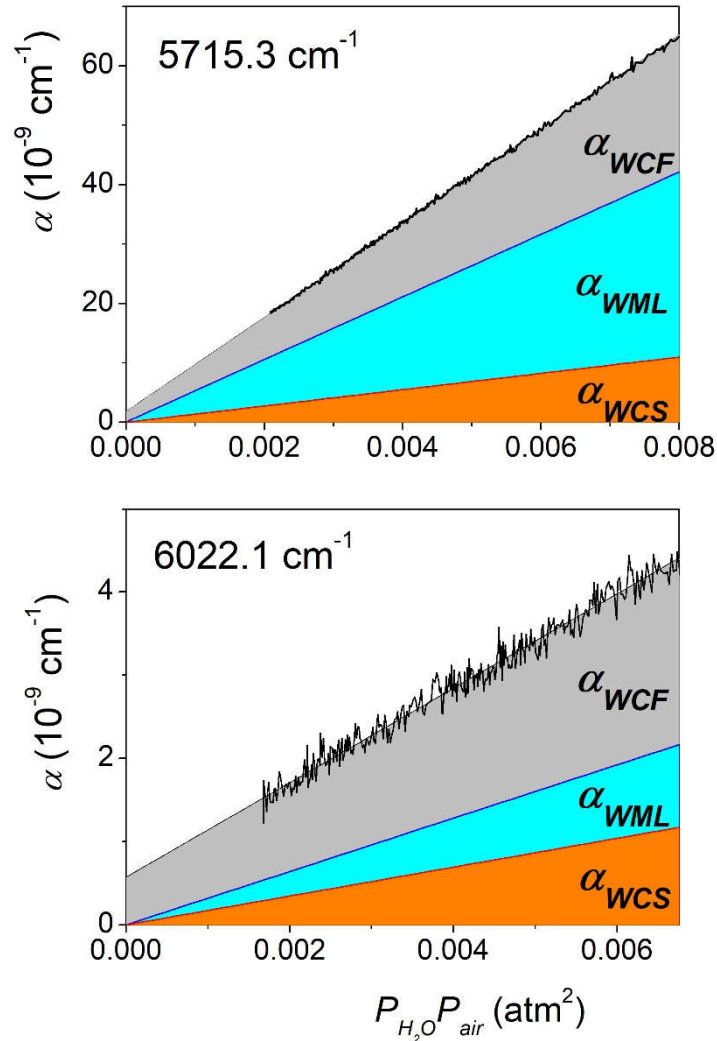
200 In a mixture of water vapor in air, the total absorption coefficient can be expressed as the sum
 201 of four terms:

$$\begin{aligned}
 202 \quad \alpha_{tot}(\nu, T) &= \alpha_{cavity} + \alpha_{WML} + \alpha_{WCS} + \alpha_{WCF} \\
 203 \quad &= \alpha_{cavity} + \alpha_{WML} + \frac{1}{kT} C_S(\nu, T) P_{H_2O}^2 + \frac{1}{kT} C_F(\nu, T) P_{H_2O} P_{air} \quad (2)
 \end{aligned}$$

204 where α_{cavity} , α_{WML} , α_{WCS} and α_{WCF} are the contributions due to the cavity, water vapor
 205 “monomer local lines” (WML), water vapor self-continuum (WCS) and foreign-continuum
 206 (WCF), respectively. C_S and C_F cross-sections are expressed in cm² molecule⁻¹ atm⁻¹.

207 From Equation (2), the foreign continuum absorption for a total pressure $P = P_{air} + P_{H_2O}$, is thus
 208 obtained by subtracting three contributions from the measured humidified air absorption
 209 (α_{tot}): the dry air signal (α_{cavity}) for the same total pressure, P , corresponding to the losses of
 210 the cavity in absence of water vapor, the contribution of the air-broadened rovibrational
 211 lines, α_{WML} , and the water vapor self-continuum absorption at the P_{H_2O} partial pressure. Note

212 that at a total pressure of 700 Torr, losses due to Rayleigh scattering in dry air and in air
 213 humidified with 1% water concentration differ by a negligible quantity of $2 \times 10^{-11} \text{ cm}^{-1}$
 214 calculated from [38].

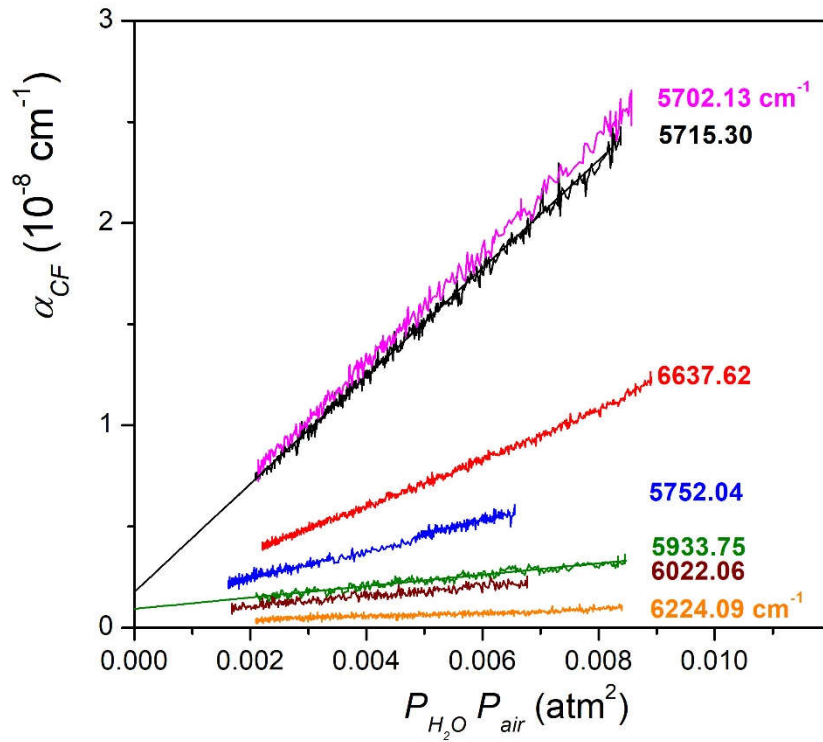


215
 216 *Figure 2. Humidified air pressure ramp recorded at 5715.30 cm^{-1} (left panel) and 6022.06 cm^{-1} (right*
 217 *panel) after subtraction of the dry air ramp (black solid line). The water monomer local contribution*
 218 *(α_{WML}), the self- (α_{WCS}) and the foreign-continuum contributions (α_{WCF}) are also plotted. The water*
 219 *relative concentration, P_{H_2O}/P_{air} , on the order of 1% was maintained constant during the pressure*
 220 *ramp.*

221 After subtraction of the baseline, the quantity $\alpha_{tot} - \alpha_{cavity} = \alpha_{WML} + \alpha_{WCS} + \alpha_{WCF}$ shows
 222 a linear dependence with $P_{H_2O}P_{air}$ as illustrated in **Figure 2**. In particular, note the linearity of
 223 $\alpha_{tot} - \alpha_{cavity}$ achieved at 6022.1 cm^{-1} confirming that the pressure effects on the mirror
 224 alignment, although important (see lower panel of **Figure 1**), is corrected by using the dry air
 225 measurements. The lines contribution was simulated at the selected spectral points, for total
 226 pressures of 350, 500, 600 and 700 Torr and the P_{H_2O} partial pressure fixed to its measured
 227 value (corresponding to about 1% concentration). Simulations were performed using the

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

238 **Figure 3** shows the achieved linear dependence of α_{WCF} versus $P_{H_2O}P_{air}$ for different
 239 selected spectral points. The change of the slope illustrates the frequency dependence of the
 240 foreign-continuum cross-sections which were derived from a linear fit (Eq.2). A small
 241 positive offset is observed at null pressure. The origin of this offset is not clear. After several
 242 tests, we only observed that the slope seems not being affected by a change of the offset
 243 value. No offset of this sort was observed in our previous measurements in the $2.3 \mu\text{m}$
 244 window [20].



245
 246 *Figure 3. Absorption coefficient of the foreign-continuum for pressure ramps obtained for different*
 247 *selected spectral points. Two linear fit are also added to show the small observed offsets.*

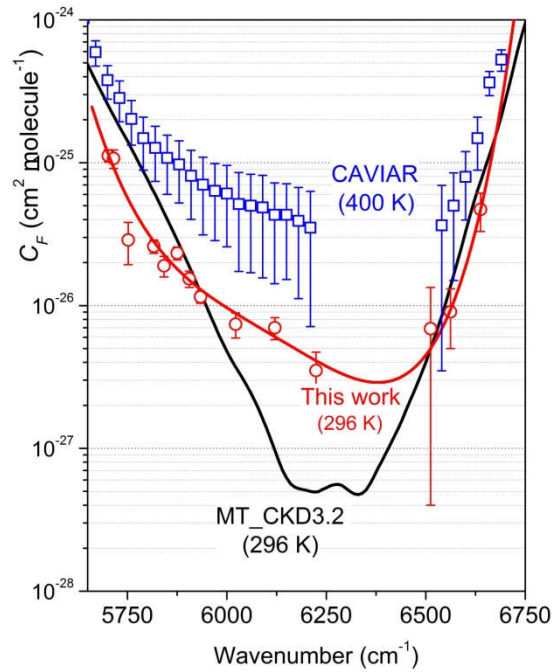
248 The C_F values derived from the procedure described above are listed in **Table 1** and presented
 249 in **Figure 4**. A 5th order polynomial fit of the C_F cross-sections (weighted by their
 250 uncertainties) is also shown in **Figure 4** and was used to provide C_F cross-sections every 10
 251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

252 *Table 1. Foreign-continuum cross-sections in the 1.6 μm window and their 1σ estimated uncertainties*
 253 *in units of the last digit (in parenthesis). The relative contributions of the “local line monomer”, self-*
 254 *and foreign continuum to the total absorption are also given in the three last columns. During the*
 255 *whole period of measurements temperature varied between 296 K and 298.5 K.*
 256

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

257

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



259

260 *Figure 4. Overview of the foreign-continuum cross-sections, C_F , in the 1.6 μm window obtained in this*
 261 *work and found in the literature. The red solid line corresponds to the fit of our data with a 5th*
 262 *polynomial. Note that for comparison purposes, the C_F values are density normalized and are given in*
 263 *$\text{cm}^2 \text{ molecule}^{-1}$.*

264 3.3 Error budget

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

270 The knowledge on the water vapour partial pressure is the main contributor to the error budget
 271 through the monomer contribution which is proportional to $P_{\text{H}_2\text{O}}$ and the self-continuum
 272 contribution proportional to $P_{\text{H}_2\text{O}}^2$. The partial pressure is derived from the fitted area of well-
 273 isolated H_2O lines with intensities reported in HITRAN2016 with uncertainties better than 2%
 274 [37]. This value is adopted as the uncertainty on $P_{\text{H}_2\text{O}}$ considering that the quality figure of the
 275 fits, defined as the ratio between peak signal and *rms* fit residuals, of several hundred, limits
 276 the error on the fitted area below 1%.

277 The monomer contribution uncertainties were determined by taking into account the error
 278 bars on the line intensities, self-broadening, air-broadening coefficients and water vapour
 279 pressure. Four simulations, $\delta_i(\nu)$, 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: $\delta\alpha_{WML}(\nu) = [\sum_{i=1}^4 \delta_i(\nu)^2]^{1/2}$.

282 The uncertainties detailed above are of type-B. To quantify statistical (type-A) uncertainties
283 we recorded consecutively six decreasing pressure ramps of humidified air at the selected
284 spectral point of 5933.75 cm^{-1} chosen because of a limited impact of the uncertainty on P_{H_2O} .
285 Between each ramp, the cell was filled again with humidified air from 350 Torr to 700 Torr
286 and two CRDS spectra were recorded to check the stability of the water concentration and
287 determine this concentration. All the ramps were base line corrected using the same dry air
288 ramp recorded just before. Nevertheless, a dry air ramp recorded just after exactly superposed
289 to the ramp used. A relative standard deviation of 2.1% was obtained on the derived C_F values
290 showing the very good short term repeatability. Two months before a C_F value 13% lower
291 than the averaged value on the 6 ramps was measured for the same spectral point with the
292 other CRDS spectrometer used in this work showing that largest statistical uncertainties have
293 to be considered. We also achieved measurements at 5842.24 cm^{-1} , 5905.72 cm^{-1} and 6369.00
294 cm^{-1} done each time at three different days. From these data we extended to each spectral
295 point a statistical uncertainty that we chosen inversely proportional to the ratio between the
296 value of α_{WCF} at 0.08 atm^2 (i.e. the maximum of the pressure ramps) and the minimum
297 detectable absorption coefficient α_{min} for the pressure ramp.
298 Combining the type-A and type-B uncertainties, we obtained the final uncertainties reported
299 in **Table 1** for each spectral point.

300

301 **4 Comparison to literature data**

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

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

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

325 Foreign-continuum provided by the latest version of the MT_CKD model (MT_CKD3.2) is
326 included in **Figure 4** for comparison purposes. No temperature dependence is provided for the
327 MT_CKD foreign cross-sections. For the low energy edge of the window, the MT_CKD C_F
328 values are significantly larger than our measurements in contrast with the values in the centre
329 of the window which are smaller by a factor of ~ 9 . Nevertheless, near the centre of the
330 window, the foreign continuum is very weak and the experimental uncertainty reaches almost
331 100%. More accurate measurements are thus required to be conclusive in the very centre of
332 the window, near 6300 cm^{-1} .

333 Finally, let us consider the humidified measurements by calorimetric interferometry reported
334 by Bicknell [22]. In the $2.3 \mu\text{m}$ window where the continuum is larger, we could calculate the
335 self-contribution to Bicknell's continuum using our determination of the C_F values and
336 obtained a good agreement with our C_S value [20]. In the considered $1.6 \mu\text{m}$ window,
337 Bicknell reported a total (self+foreign) continuum absorption coefficient of $3.2 \times 10^{-8} \text{ cm}^{-1}$ at
338 6150 cm^{-1} for a mixture of 18.75 Torr of H_2O in N_2 with a total pressure of 760 Torr (see [10]
339 for details). For the same experimental conditions, we calculate an absorption coefficient of
340 $\sim 1 \times 10^{-8} \text{ cm}^{-1}$ when using our present C_F determination of $5.4(9) \times 10^{-27} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$ and
341 a C_S value of $4.9(7) \times 10^{-25} \text{ cm}^2 \text{ molec}^{-1} \text{ atm}^{-1}$ from Ref. [20]. This difference by a factor of 3 is
342 outside the combined error bars and difficult to interpret on the basis of the scarce
343 experimental information provided in Ref.[22] (see [39] for discussion). Note that our C_F
344 determinations rely on careful study of the pressure dependence of the continuum signal while
345 Bicknell's measurements were performed at a single pressure [22].

346 **5. Conclusion**

347 Water vapor foreign-continuum cross-sections have been obtained at room temperature in the
348 1.6 μm window. The corresponding small cross-sections were derived from CRDS
349 measurements during pressure ramps recorded at fixed spectral points between 5700 cm^{-1} and
350 6640 cm^{-1} . Fifteen spectral points were selected to sample the window at frequencies
351 corresponding to small contribution of the water monomer lines. The CAVIAR measurements
352 at high temperature in the same window are larger in amplitude but show a similar
353 wavelength dependence.

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

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

374

375 **Acknowledgments**

376 This project is supported by the Labex OSUG@2020 (ANR10 LABX56) and the LEFE-ChAt
377 program from CNRS-INSU.

- [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 H₂O 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 H₂O 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.jqsrt.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 μm 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 dependence 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, Čermák 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 foreign-continua 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 μm 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 $\text{H}_2\text{O}+\text{N}_2$ 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. $\text{H}_2\text{O} \text{ N}_2$ collision-induced 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 Lafferty WJ. 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, Radel 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 $5 \times 10^{-13} \text{ cm}^{-1}$ 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, Weislo P, Yu S, Zak EJ. The HITRAN2016 Molecular Spectroscopic Database. *J Quant Spectrosc Radiat Transf* 2017;203:3-69. doi: 10.1016/j.jqsrt.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