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Key words

Water vapor; continuum absorption; MT_CKD model; OFCEAS; transparency window; atmosphere

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Abstract

Measurements of the water vapor absorption cross-sections at two spectral points of the 2.1 µm and 4.0 µm transparency windows are performed by optical feedback cavity enhanced absorption spectroscopy (OFCEAS).

The self-continuum cross-section, C_S, is measured for temperature values of 30 and 47 °C (303 and 320 K) at the 2853 cm^{-1} spectral point, corresponding to the lowest opacity region of the 4.0 µm transparency window. The C_S values derived from the pressure squared dependence of the self-continuum, are found consistent with previous CEAS measurements in the considered window but significantly smaller than measurements by Fourier transform spectroscopy (FTS). The C_S temperature dependence is discussed in relation with FTS measurements at high temperature.

Foreign-continuum cross-sections, C_F, are newly obtained from OFCEAS spectra of moist air in flow regime at the 4302 cm^{-1} spectral point of the low energy edge of the 2.1 µm window. After subtraction of the monomer and self-continuum contributions, C_F values are derived from the linear variation of the foreign-continuum absorption with the product of the water vapor and air partial pressure. The measurements were performed for temperature values of 34 and 47 °C (307 and 320 K) and no significant temperature variation is evidenced. The present C_F value at 4302 cm^{-1} is gathered with previous CEAS measurements at seven spectral points of the 2.1 µm window. This consistent set of C_F values is used to derive from a polynomial fit, the empirical frequency dependence of $C_F(\nu)$ over the 4250-5000 cm^{-1} range. Overall, the semi-empirical MT_CKD_3.5 values of C_F are significantly underestimated in the centre of the considered window.

1. Introduction

Water vapor is the first greenhouse gas of our atmosphere. Its absorption represents between 50 and 70 % of the incoming solar light. The absorption spectrum of water vapor consists of narrow absorption lines due to transition between ro-vibrational levels of the water molecule and a more featureless continuum whose interpretation remains a major controversy in molecular spectroscopy [1]. The water spectrum is organized in bands of strong absorption, interspersed with a number of more transparent "windows". Although its amplitude is smaller in the windows, the relative importance of the continuum is much higher than in the band regions where the line absorption generally dominates.

The insufficient knowledge of the water continuum in the near infrared transparency windows makes it an important source of uncertainty for the radiative budget of the Earth's atmosphere. As a result of the lack of accurate experimental data, the semi-empirical MT_CKD model [2-4] is generally implemented in atmospheric radiative transfer codes. This model uses an empirical line shape modeling with sub-Lorentzian far wings and a *weak interaction* term between a water vapor molecule and another molecule for the intermediate wings. The parameters of this profile are then fitted to few laboratory or field measurements available mostly in the mid infrared.

Indeed, the quantitative determination of weak absorption continua is generally challenging by transmission spectroscopy (like Fourier transform spectroscopy (FTS)) as the continuum shows up as a small decrease of the transmitted spectrum baseline. The challenge is made even more difficult in the case of water vapor because of possible surface effects on the optics of the experimental setup. During the last decade, large experimental efforts have been performed to complete the pioneer works of Burch [5-7] in the transparency windows. FTS allowed for large spectral coverage [8-10] and provided self-continuum cross-sections significantly higher than the generally adopted MT_CKD values in the 4.0, 2.1 and 1.6 µm windows. These FTS measurements were not confirmed by our recent series of experiments using cavity enhanced absorption spectroscopy (CEAS) [11-18], namely cavity ring down spectroscopy (CRDS) and optical feedback–cavity enhanced absorption spectroscopy (OF-CEAS). These CEAS measurements, supported by a clear pressure squared dependence of the continuum absorption, have been recently used to constrain the MT_CKD self-continuum in the 4.0, 2.1, 1.6 and 1.25 µm windows.

In the case of the foreign-continuum arising from interactions between water molecules and molecular oxygen and nitrogen, experimental data are even more scarce in particular at room temperature [20]. Regarding the transparency windows, cross-sections provided by FTS [21-23] in the mid-IR windows and by cavity ring down spectroscopy (CRDS) in the 2.1 µm window [16] have led to a significant increase of the MT_CKD foreign-continuum since the 2.8 version [3].

The temperature dependence of the self- and foreign-continua is of importance for atmospheric applications. The self-continuum is known to have a strong negative dependence around room temperature while the foreign-continuum is believed to be much less sensitive to the temperature. Note that the temperature dependence may help to discriminate different processes responsible of the

continuum: far wings of the rovibrational lines, "water dimers" – and other bimolecular complexes, such as O_2-H_2O and N_2-H_2O, and collision-induced absorption (CIA).

The present work is a further step in our experimental investigation of the water self- and foreign-continua by CEAS. While the FTS technique allowed for wide spectral coverage, laser based techniques are inherently more sensitive but generally limited to narrow spectral intervals depending of the availability of laser sources. Here, we report on new OFCEAS self-continuum cross-section, C_S, at 30 and 47 °C at the 2853 cm^{-1} spectral point in the center of the 4.0 µm transparency window and foreign-continuum cross-sections, C_F, at the 4302 cm^{-1} spectral point of the low energy edge of the 2.1 µm window at 34 and 47 °C. In the following part 2, we will present the experimental procedure and data acquisition adopted for the two series of measurements. Parts 3 and 4 are devoted to the retrievals of the values of C_S at 2853 cm^{-1} and C_F at 4302 cm^{-1}, respectively and include a discussion of the comparison with literature data and of the temperature dependence. For the convenience of the reader, we have gathered in **Table 1**, the previous and present CEAS measurements of C_S in the 4.0 µm window and C_F in the 2.1 µm window.

Table 1. Summary of the CEAS measurements of self-continuum cross-sections, C_S, in the 4.0 µm window and foreign-continuum cross-sections, C_F, in the 2.1 µm window. Number in parenthesis correspond to 1σ uncertainty in units of the last digit.

Window Approx. center	Spectral point (cm^{-1})	*T(K)*	C_S (10^{-23} cm^2 $molecule^{-1}$ atm^{-1})	*Reference*
2700 cm^{-1} (4.0 µm)	2283 (4.38 µm)	296.15	1.26(6) [a]	*Campargue et al. 2016 [13]*
		301.15	1.18(6) [a]	
		312.15	0.88(4) [a]	
	2491 (4.014 µm)	297.3	0.41(3)	*Richard et al. 2017 [14]*
		312.3	0.305(43)	
		325.6	0.260(37)	
	2853 (3.5 µm)	**303.15**	**0.585(42)**	***This work***
		320.15	**0.428(39)**	
	3007 (3.3 µm)	298.15	1.96(39)	*Lechevallier et al. 2018 [15]*
		303.15	2.17(54)	
		308.15	1.83(46)	
		313.15	1.43(36)	
		318.15	1.82(46)	
		323.15	1.40(35)	
4700 cm^{-1} (2.1 µm)			C_F (10^{-25} cm^2 $molecule^{-1}$ atm^{-1})	
	4248.83	297	3.91(40) [b]	*Mondelain et al. 2015 [16]*
	4257.30		3.93(30) [b]	
	4302	**307.15**	**2.75(17)**	***This work***
		320.15	**2.60(18)**	
	4432.6	297	1.26(5)	*Vasilchenko et al. 2019 [17]*
	4436.3		1.15(5)	
	4522.0		0.810(36)	
	4724.1		0.444(43)	
	4999.0		0.83(18)	

Notes

[a] *Total uncertainty of 5% [13]. The (smaller) error bars given in Table 2 of Ref. [13] are limited to the fit uncertainty*

[b] *Total uncertainty of 30% [16]. The (smaller) error bars given in Table 2 of Ref. [16] are limited to the fit uncertainty.*

2. Experimental setup

a. OF-CEAS spectrometers

OFCEAS is a high-sensitivity technique which relies on optical feedback to efficiently inject the probe laser into a high-finesse V-shaped cavity [24,25]. This technique has been used to measure water continua in other spectral regions [13-15, 18]. The reader is referred to [18] for a more detailed description. The use of a V-shaped cavity allows reinjecting part of the resonant intra-cavity field into the diode laser source. This optical feedback leads to laser emission width narrowing and a temporary locking of the laser frequency to the cavity mode, improving the efficiency of the cavity injection. Due to the fixed geometry of the cavity, the spectra have an intrinsically linear frequency scale with point spacing equal to the free spectral range (FSR). Both arms of the cavity have a nominally 40 cm length, corresponding to an FSR of 187.5 MHz. Applying a ramp on the diode laser current while keeping its temperature constant, spectra can be recorded over more than 100 cavity modes (~0.6 cm^{-1}) at a rate of about 5 Hz. Transmission spectra are obtained by dividing the maximum output of the cavity at each mode by a reference photodiode signal, while a single ring down event is recorded at the end of each scan to retrieve the absolute absorption coefficient [26].

Two distinct OFCEAS spectrometers were used for the two spectral ranges covered in this work. In one setup, the probe laser was an interband cascade laser (ICL) tunable from 2850 cm^{-1} to 2856 cm^{-1}, and the baseline ring down time was 13 µs corresponding to a mirror reflectivity of 99.990 %. The other setup used a distributed feedback (DFB) laser diode emitting around 4300 cm^{-1} and mirrors of reflectivity 99.997 % as determined from the baseline ring down time of 45 µs.

For both setups, the cavity temperature was monitored with a thermistor of 0.3 K accuracy, and could be controlled between about 30 and 50 °C by heating bands regulated *via* a PID loop.

The baseline RMS noise was about 1×10^{-9} cm^{-1} for the 4302 cm^{-1} setup. For the 2853 cm^{-1} setup, there was an additional, unexplained noise at higher temperature, so that the base line RMS noise ranged from about 5×10^{-9} cm^{-1} at 30 °C, to 1.6×10^{-8} cm^{-1} at 47 °C. In all cases, 100 spectra were averaged at each data point.

b. Self-continuum data acquisition

For the self-continuum measurements at 2853 cm^{-1}, a steel tank filled with deionised water was connected upstream of the cavity. A needle valve at the inlet of the cavity allowed adjusting the flow at a value of 3 to 4 sccm. At the outlet, an electrovalve was used to control the intra-cavity pressure, which was monitored with a Wika sensor (250 mbar full scale) calibrated against a MKS sensor (10 mbar range, 0.25 % accuracy).

A flow of water vapor through the cavity was initialized at a pressure of 20 mbar. Spectra were recorded at this pressure value, then the pressure was stepped down to approximately 5 mbar, before bringing it back up to 20 mbar. For each of those nine pressure steps, 100 spectra were averaged. This procedure was repeated for two temperature values: 30 °C and 47 °C. **Figure 1** shows spectra recorded at 10, 15

and 20 mbar, for both temperature values. The rapid increase of the continuum with pressure and the significant decrease with temperature are clearly observed.

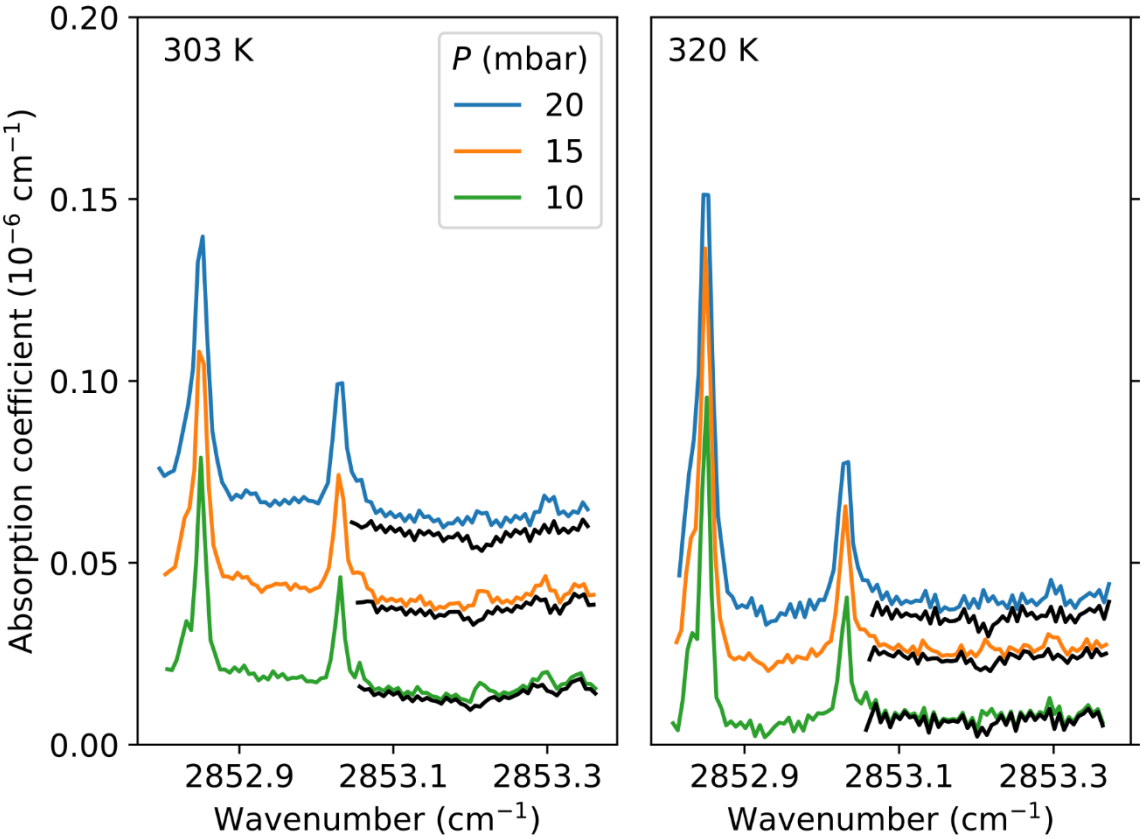

Figure 1: *Spectra recorded with pure water vapor at three pressure values, for two temperature conditions. Black lines denote the monomer-corrected spectra used to determine the self-continuum absorption. The constant term due to the empty cavity losses, obtained from the fit (see section 3a) was subtracted.*

c. Foreign continuum data acquisition

A commercial humidity generator (from Omicron Technologies) was used to generate moist air for foreign continuum measurements. This generator is based on a temperature regulated membrane system to generate pure water vapor which is then mixed with the dry carrier gas (Alphagaz^{TM}2 synthetic air from Air Liquide) with a proportional control solenoid valve with bypass to achieve the desired humidity level, monitored via the dew point temperature measured by a chilled mirror hygrometer (Michell Instruments). A flow controller and back pressure controller (both from Bronkhorst) regulated the gas flow (300 sccm) and the pressure (1045 mbar) in the exit. A part of this flow (about 10 sccm) was derived into the OFCEAS high-finesse cavity through another flow controller, while the intra-cavity pressure was stabilized to a value of 510 Torr (680 mbar) by a Bronkhorst pressure controller at the outlet.

The recording procedure was the following. First, dry nitrogen gas was flowed through the cavity at the same pressure value of 510 Torr to record the baseline cavity mirror losses. The gas source was then

switched to the moist air, and once the absorption in the cavity had reached a stable state (reflecting stability of the water mole fraction), 100 spectra were averaged before changing the water mole fraction set point to the next value. This procedure was repeated for two temperature values: 34 °C and 47 °C, and four water mole fraction values: 5000, 10000, 12500 and 15000 ppmv.

3. Self-continuum at 2853 cm^{-1}

In a cell filled with pure water vapor, the total absorption coefficient can be expressed as the sum of three terms:

$$\alpha_{tot}(\nu, T) = \alpha_{cavity} + \alpha_{WML} + \alpha_{WCS} \quad (2)$$

where α_{cavity}, α_{WML}, α_{WCS} are the contributions due to the cavity, water vapor "monomer local lines" (WML), and water vapor self-continuum (WCS), respectively. Note that the contribution of Rayleigh scattering is negligible. The cross-section C_S, expressed in cm^{2}molecule^{-1}atm^{-1}, is defined by $\alpha_{WCS} = \frac{1}{kT} C_S(\nu, T) P_{H_2O}^2$, where k is the Boltzmann constant and P_{H_2O} is the water vapor pressure.

a. Data analysis

The absorption due to the monomer lines was subtracted using the line-by-line fitting program MATS [27]. The water vapor transitions, as well as a few formaldehyde lines which were visible in the spectrum, were modeled from HITRAN2016 [28] parameters by Voigt profiles truncated at ±25 cm^{-1} from the line center. The formaldehyde concentration was fitted and estimated to be on the order of 10 ppb. The HDO concentration was assumed to be 20 % lower than the natural abundance from HITRAN. The monomer-corrected values were averaged over a 0.3 cm^{-1} wide part of the scan which is not much affected by the monomer lines (50 points near 2853.25 cm^{-1}, shown in black in **Fig. 1**). The obtained data points are plotted in **Fig. 2** as a function of the squared pressure, with error bars corresponding to combined uncertainties including both statistical (type A) and type B uncertainties. Type B contributions to the uncertainty include the baseline uncertainty (2×10^{-9} cm^{-1}), and the uncertainty on the monomer lines, which is calculated by propagating the HITRAN error bars on the line intensities and self-broadening coefficients. Two simulations were performed, increasing either all intensities or all γ_{self} values by their HITRAN error bars, yielding deviations from the usual HITRAN simulation which were then added in quadrature.

The slope of a linear regression yields the self-continuum cross-section C_S. The intercept of this regression corresponds to the empty-cavity losses α_{cavity} and was subtracted in **Fig. 2**. The values given by the fit are reported here along with the fit uncertainty: $5.85(42)\times10^{-24}$ cm^{2}molecule^{-1}atm^{-1} at 303 K, $4.28(39)\times10^{-24}$ cm^{2}molecule^{-1}atm^{-1} at 320 K.

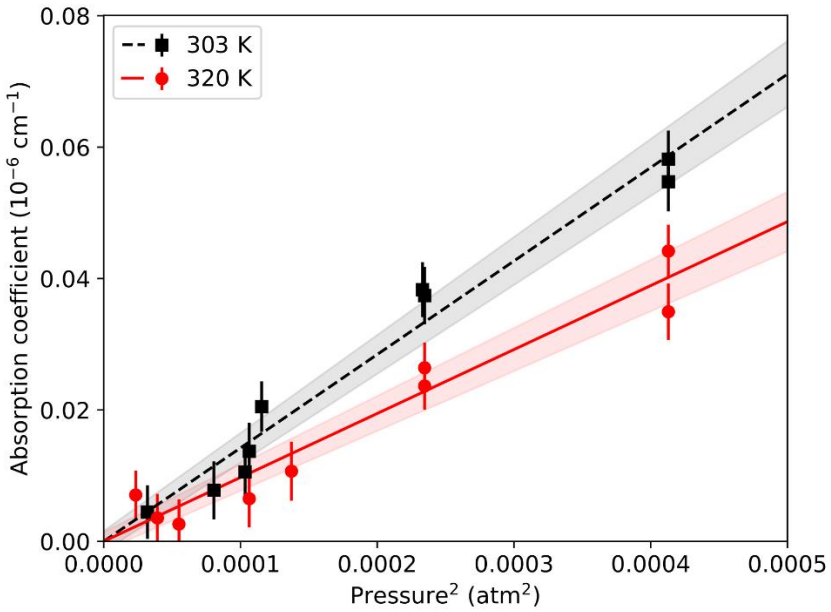

Figure 2: *Self-continuum absorption* α_{WCS} *as a function of squared pressure, for two temperature values. The self-continuum cross-section is obtained as the slope of the linear fits. The constant term due to the cavity losses, obtained from the fit was subtracted, and shaded areas depict the fit uncertainty.*

b. Comparison to literature

The different experimental determinations of the self-continuum cross-sections near room temperature in the 4 µm window are plotted in **Fig. 3** together with some recent versions of the MT_CKD continuum up to the current 3.5 version. Four datasets using long-path absorption cells and covering most of the transparency window were published prior to our series of OFCEAS measurements. In 1984, Burch and Alt retrieved the continuum between 2400 and 2640 cm^{-1} using a grating spectrograph and a pathlength of 707 m [5,6]. An optical configuration which allowed changing the number of passes through the absorption cell without perturbing the optical alignment was adopted to minimize the spectra baseline drifts. The three other studies were performed by FTS: *(i)* the CAVIAR consortium performed room temperature measurements at the Rutherford Appleton Laboratory with a 512.7 m pathlength [8], *(ii)* a similar FTS approach with a pathlength of 612 m at 289.5 and 287 K, was adopted at the Institute of Atmospheric Optics in Tomsk [9,10], *(iii)* finally, Baranov and Lafferty, from NIST, reported FTS measurements between 311 and 363 K with a 100 m pathlength [29].

The OFCEAS measurements are limited by the availability of diode laser sources. Previous OFCEAS studies were performed at 2283 cm^{-1} [13], 2491 cm^{-1} [14] and 3007 cm^{-1} [15] (see **Table 1)**. The present measurement at 2853 cm^{-1} completes the sampling of the window and is found consistent with previous OFCEAS values. The comparison to the FTS values is similar to that encountered in most of the transparency windows: although reported with large error bars, the FTS values are significantly larger than the laser measurements. Strictly speaking, only CAVIAR [8] and NIST [29] measurements are available for comparison near 2850 cm^{-1}, Tomsk measurements [9,10] showing a gap in the 2800-3050 cm^{-1} interval. Although the CAVIAR and NIST C_S values of $5.0(3.2)\times10^{-23}$ and $2.6(6)\times10^{-23}$

$cm^2molecule^{-1}atm^{-1}$ were reported with 65% and 23% error bars, respectively, the OFCEAS value of $5.85(42)\times10^{-24}$ $cm^2molecule^{-1}atm^{-1}$ falls outside the (1σ) FTS error bars.

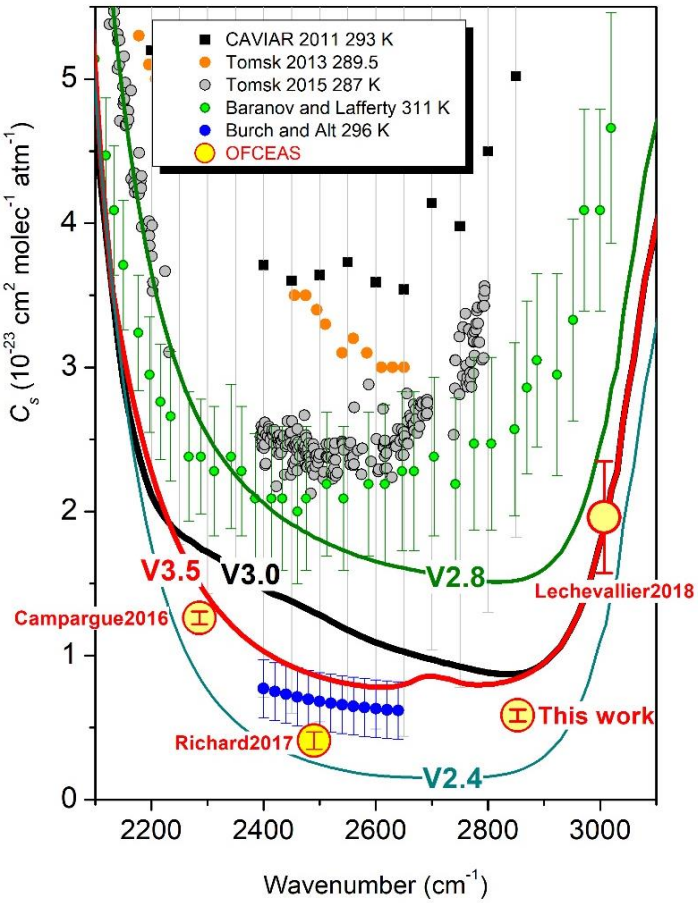

Figure 3: *Overview comparison of the self-continuum cross-section of water vapor near room temperature in the 4.0 µm window. Solid lines show different versions of the MT_CKD model at 296 K [2-4]. Experimental results were obtained by OFCEAS, (red circles; Campargue et al. [13]; Richard et al. [14]; Lechevallier et al. [15]; this work); by FTS from Baranov and Lafferty [29]) (light green circles), from CAVIAR (black squares; Ptashnik et al. [8]), from Tomsk2013 (orange circles; Ptashnik et al. [9]), from Tomsk2015 (green circles; Ptashnik et al, [10]) and with a grating spectrograph by Burch and Alt [5,6] (dark blue circles). Note that the plotted experimental results correspond to different temperature values (see values given in the insert). The temperature of the OFCEAS results are 296.15, 297.3, 298.15, and 303.15 K, for Campargue et al. [13]; Richard et al. [14]; Lechevallier et al. [15], and this work, respectively. The 30-50 % error bars on Tomsk2013 and Tomsk2015 values are not plotted for clarity.*

Over the last ten years, the different versions of the MT_CKD model in the center of the 4.0 µm window varied over one order of magnitude (**Fig. 3).** On the basis of the OFCEAS measurement at 2283 cm^{-1} [13], the MT_CKD 3.5 version of the self-continuum has been recently decreased in the low energy edge of the window. At the 2853 cm^{-1} point of present interest, the MT_CKD_V3.5 C_S value (8.73×10^{-24} $cm^2molecule^{-1}atm^{-1}$) is larger than the OFCEAS value by about 50 %. Similar and even more pronounced overestimation was noted at the 2490 cm^{-1} spectral point [14], indicating that in the very center of the window, the MT_CKD_V3.5 C_S values should be significantly decreased. It is interesting to note that the pioneer results of Burch and Alt in the 2400-2640 cm^{-1} are the only previous measurements in reasonable agreement with OFCEAS values in this region.

c. Temperature dependence

Atmospheric modeling requires the knowledge of the temperature dependence of the water vapor self-continuum in particular at room temperature and below. Although the water self-continuum cross-section is decreasing rapidly with temperature (about 36% for a temperature variation of 17 K presently measured at 2853 cm^{-1}), it is easier to measure the continuum at high temperature where larger saturation pressures allow for increasing considerably the water vapor pressure. For instance, the CAVIAR consortium reported measurements at temperatures from 350 to 472 K using a short-path absorption cell and vapor pressure values up to 1.6 atm [8]. We have collected in **Fig. 4**, the C_S values available in the literature at different temperatures around our measurement points at 2853 cm^{-1} and plotted them in logarithmic scale *versus* 1/*T*. In addition to the CAVIAR room and high temperature measurements, the NIST data [29] cover the 311-363 K range.

The overall distribution of the experimental C_S values is very similar to what was observed at several spectral points of the 4.0 and 2.1 µm windows (see Fig.7 of Ref. [15], Fig.6 of Ref. [14], Fig. 6 of Ref. [18]), our two present C_S values are on line with the high temperature CAVIAR values while CAVIAR room temperature value (obtained with a different FTS cell) is strongly overestimated. As already noted for other spectral points, the OFCEAS and the CAVIAR high temperature values follow a simple exponential law in 1/*T* with a slope close to the dissociation energy of the water dimer, $D_0 \approx 1100$ cm^{-1} [30].

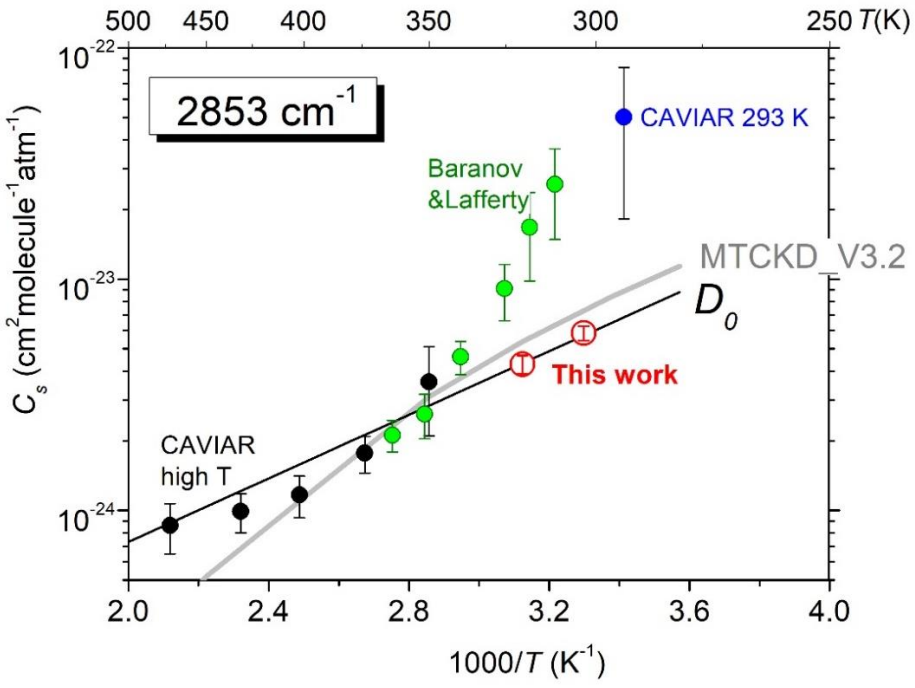

Figure 4: *Temperature dependence of the water vapor self-continuum cross-sections near 2853 cm^{-1} obtained by OFCEAS (open red circles), by FTS (CAVIAR at high temperature [8] (green squares): CAVIAR at room temperature [8] (full blue circle): Baranov and Lafferty [29] (full green circles). The MT_CKD_V3.5 values which are normalized to the number density at 1 atm and 296 K were multiplied by 296/T. The D_0 slope corresponds to an exp(D_0/kT) function, $D_0 \approx 1100$ cm^{-1} being the dissociation energy of the water dimer molecule.*

The MT_CKD_V3.5 temperature dependence at 2853 cm^{-1} included in **Fig. 4** shows a behavior close to the $\exp\left(\frac{D_0}{kT}\right)$ function near room temperature while at higher temperature, the MT_CKD self-continuum is decreasing more rapidly than observed from the high temperature CAVIAR measurements.

4. Foreign continuum at 4302 cm^{-1}

As mentioned above, the foreign-continuum measurements were performed at a constant total pressure of 510 Torr, for two temperature values (34°C and 47°C) and four water mole fraction values of 5000, 10000, 12500 and 15000 ppmv.

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

$$\alpha_{tot}(\nu,T) = \alpha_{cavity} + \alpha_{WML} + \alpha_{WCS} + \alpha_{WCF}$$
$$= \alpha_{cavity} + \alpha_{WML} + \frac{1}{kT} C_S(\nu,T) P_{H_2O}^2 + \frac{1}{kT} C_F(\nu,T) P_{H_2O} P_{air} \quad (3)$$

where, in comparison to Eq. (2), the additional term α_{WCF} denotes the contribution due to the foreign-continuum (WCF), with C_F expressed in $cm^2 molecule^{-1} atm^{-1}$. P_{H_2O} and P_{air} are the water vapor and dry air partial pressures, respectively. Due to the negligible difference (~10^{-11} cm^{-1}) in Rayleigh scattering losses between the pure nitrogen baseline measurements and the moist air measurements at the same pressure, the Rayleigh contribution was omitted from Eq. (3).

a. Data analysis

In a first step, the baseline absorption α_{cavity}, measured while flowing the cavity with pure N_2 at the same nominal pressure as the water mixture measurements (510 Torr), was subtracted from each spectrum. **Figure 5** shows the various contributions to the remaining absorption for two values of the water vapor molar fraction. The absorption due to the water monomer lines was calculated from HITRAN2016 parameters using Voigt profiles truncated at ±25 cm^{-1} from the line center without including the pedestal. The isotopic abundance of HDO was reduced by 20% as compared to the HITRAN natural abundance. There were no observable lines from other species.

In this spectral region the self-continuum cross-section has been measured in a previous work [18], over a temperature range comprising the temperatures studied here. We interpolated the reported C_S values from Ref. [18] to calculate the self-continuum absorption at our experimental conditions (C_S values of 1.88×10^{-23} and 1.55×10^{-23} cm^2 $molecule^{-1}$ atm^{-1} were used at 34 °C and 47 °C, respectively). Obviously, the total pressure being identical, the relative contribution of the self-continuum is larger for the higher mole fractions (see **Fig. 5**).

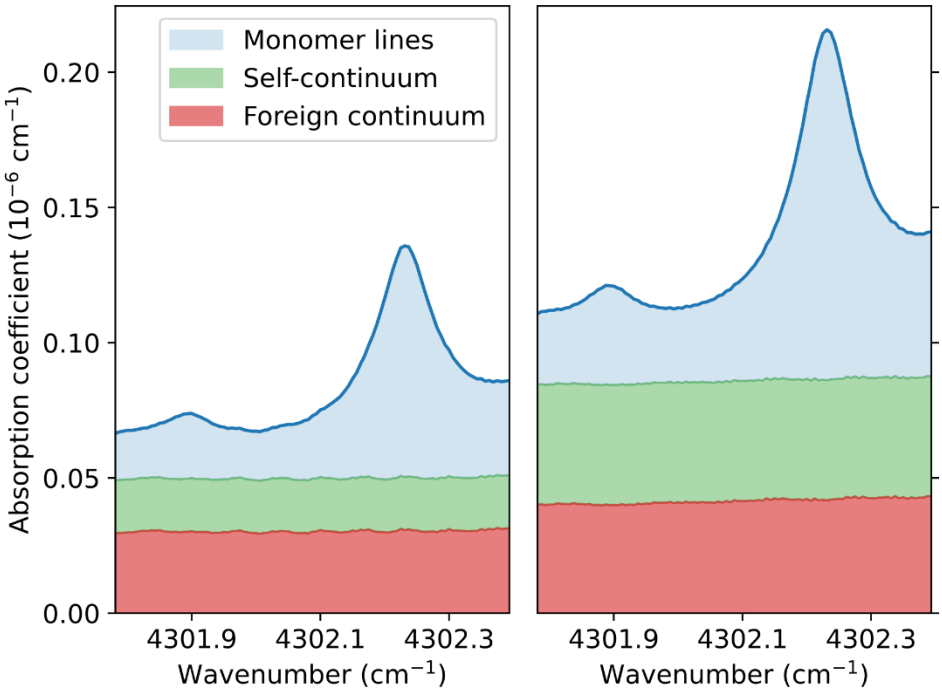

Figure 5: *Baseline-corrected spectra recorded for two water vapor molar fractions (left: 10 000 ppmv, right: 15 000 ppmv), at a temperature of 307 K. The total pressure was 510 Torr. The shaded areas show the absorption due to local monomer lines (in blue), the self-continuum (in green) and the foreign continuum (in red). Note that the self-continuum absorption grows faster than the other two contributions with the water vapor molar fraction, reflecting its quadratic dependence on water vapor density.*

Type B uncertainties were calculated from Eq. (3) by error propagation. The uncertainty on the baseline absorption α_{cavity} is taken to be 1×10^{-9} cm^{-1}, while a 2% uncertainty is estimated for the water vapor pressure determined from the hygrometer reading. The monomer contribution uncertainty was determined by propagating the HITRAN error bars of the line intensities, self-broadening and air-broadening coefficients, as well as the water vapor partial pressure uncertainty. Four simulations were performed, each of them with either the intensities, γ_{self}, γ_{air} coefficients or P_{H_2O} values increased by their error bar, yielding deviations $\delta_i(\nu)$ from the usual HITRAN simulation. The uncertainty on α_{WML} was obtained as $\delta\alpha_{WML}(\nu) = \left[\sum_{i=1}^{4}\delta_i(\nu)^2\right]^{1/2}$. The C_S uncertainty was taken from Ref. [18].

The values of α_{WCF} were averaged over the extent of the 0.6 cm^{-1} wavenumber range of each scan. The average values are plotted in **Fig. 6** as a function of the product of the water vapor pressure P_{H_2O} and air pressure P_{air}. The error bars on this plot show the combined uncertainty including both the statistical (type A) uncertainty given by the standard deviation of the averaged spectral points, and the type B uncertainty described above.

The slope of a linear fit, weighted by the inverse of the variance of each point, gives the foreign continuum cross-section C_F. The values derived from the fits are reported here along with the fit uncertainty: $2.75(17)\times10^{-25}$ cm^{2}molecule^{-1}atm^{-1} at 307 K, $2.60(18)\times10^{-25}$ cm^{2}molecule^{-1}atm^{-1} at 320 K. The small temperature difference of 13 K between our two series of measurements does not allow to

evidence a significant variation and we can merely confirm that the foreign-continuum has a small temperature dependence.

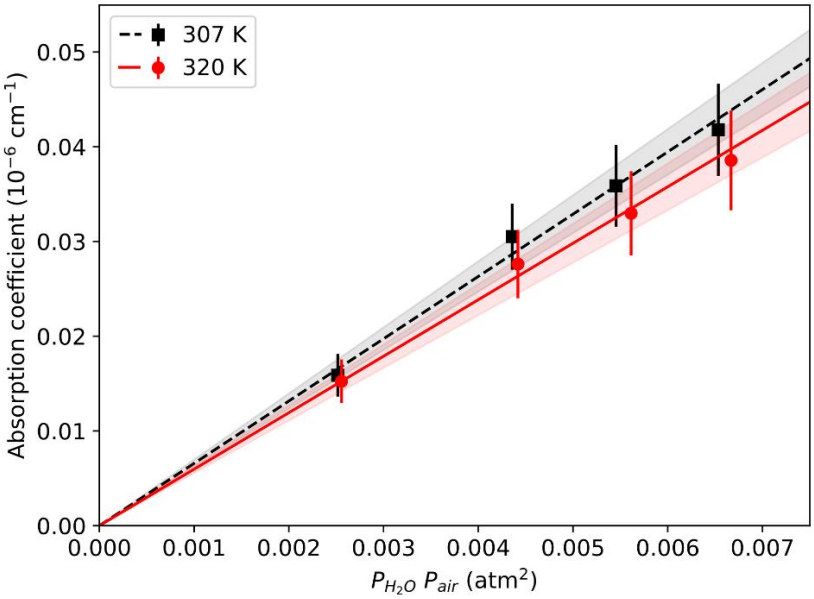

Figure 6: *Foreign continuum absorption* $\boldsymbol{\alpha_{WCF}}$ *as a function of the product of water vapor and air pressures, for two temperature values. The error bars shown here correspond to the combined uncertainty including both type A and type B uncertainties. The slopes of linear fits, also plotted, give the foreign continuum cross-sections* C_F*. Shaded areas show the uncertainty on the fitted slopes.*

b. Comparison to literature

The comparison of the available experimental determination of the foreign-continuum cross-sections in the 2.1 µm window to the MT_CKD_V3.5 values is presented in **Fig. 7**. Experimental data at room temperature are limited to the present OFCEAS determination at 4310 cm^{-1}, the CRDS data points at 4250 cm^{-1} [16] and at 4433, 4436, 4522, 4724 and 4999 cm^{-1} [17]. The CAVIAR consortium reported foreign-continuum absorption by FTS between 1.1 and 5 µm at high temperatures (350-431 K) with an absorption path length of 17.7 m [31]. The chosen elevated temperatures allowed for increasing the water vapor partial pressure of the recordings between 266 and 600 mbar. Compared to our measurement conditions, these high water vapor pressure values combined with air pressure of about 4 atm led to an increase of the foreign-continuum absorption signal by two or three orders of magnitude. The FTS recordings between 350 and 431 K did not reveal temperature dependence greater than the uncertainty in those measurements. The C_F values included in **Fig. 7** are those reported by Ptashnik et al. at the 400 K average temperature [31].

The CRDS and OFCEAS C_F cross-sections values represent a consistent dataset which can be reproduced by a 4th order polynomial fit (see Fig. 7) - the corresponding polynomial coefficients are given in the figure caption.

Overall the present OFCEAS and previous CRDS room temperature C_F values are systematically below the CAVIAR values (at 400 K) by a factor between 2 and 4. In the center of the window, the FTS relative uncertainties are very large (up to 93 %) which makes the CRDS value at 4724 cm^{-1} fall within the 1σ FTS confidence interval. This is not the case on the low energy edge of the window. For instance at the 4302 cm^{-1} spectral point presently measured, CAVIAR C_F value is $5.8(2.2)\times10^{-25}$ $cm^2molecule^{-1}atm^{-1}$ to be compared to an OFCEAS value of $2.75(6)\times10^{-25}$ $cm^2molecule^{-1}atm^{-1}$ at 307 K (the corresponding density normalized C_F values are 7.8(3.0) and 2.85(6) $cm^2molecule^{-1}atm^{-1}$). If the CAVIAR values at 400 K are confirmed, it would indicate that the foreign-continuum exhibits significant *positive* temperature dependence.

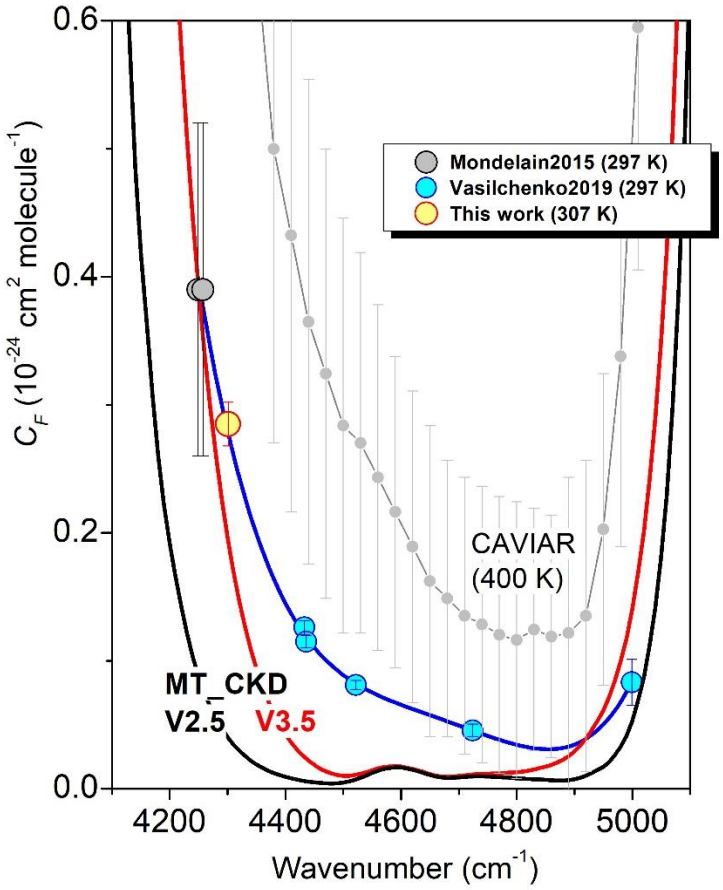

Figure 7. *Overview of the experimental foreign-continuum cross-sections, C_F, reported in the literature and retrieved in this work (red circle) for the 2.1 µm window and comparison to the MT_CKD model in its versions 3.5 (red) and 2.5 (black). Previous experimental determinations are the CAVIAR FTS values at 400 K from Ref. [31] (full grey circles) and the CRDS values (light blue circles) from Vasilchenko et al. [16] at 4250 cm^{-1}) and from Mondelain et al. [17] at 4433, 4436, 4522, 4724, 4999 cm^{-1}. Note that for comparison purposes, the C_F values are density normalized and are given in cm^2 $molecule^{-1}$ (density normalized C_F values in cm^2 $molecule^{-1}$ correspond to C_F values in cm^2 $molecule^{-1}$ atm^{-1} multiplied by the factor T/296). The blue solid line corresponds to the fit of the CRDS and OFCEAS data with a 4^{th} order polynomial: $3.99039496\times10^{-21}-3.41093025\times10^{-24}\nu+1.09342553\times10^{-27}\nu^2-1.55784737\times10^{-31}\nu^3+8.32287078\times10^{-36}\nu^4$ where ν is the wavenumber in cm^{-1}.*

The MT_CKD_V3.5 foreign-continuum included in **Fig. 7** is assumed to be temperature independent. The MT_CKD foreign-continuum was recently increased in the 2.1 µm window, taking into account our CRDS value at 4250 cm^{-1} [17] and the NIST values [29] in the 4.0 µm window (the MT_CKD_2.5 is

included in **Fig. 7**, for comparison). On the low and high energy range of the window, the agreement with CRDS and OFCEAS values has become reasonable but the MT_CKD foreign-continuum should be significantly increased in the centre of the window (by a factor of about 5 for the minimum C_F values near 4700 cm^{-1}).

5. Conclusion

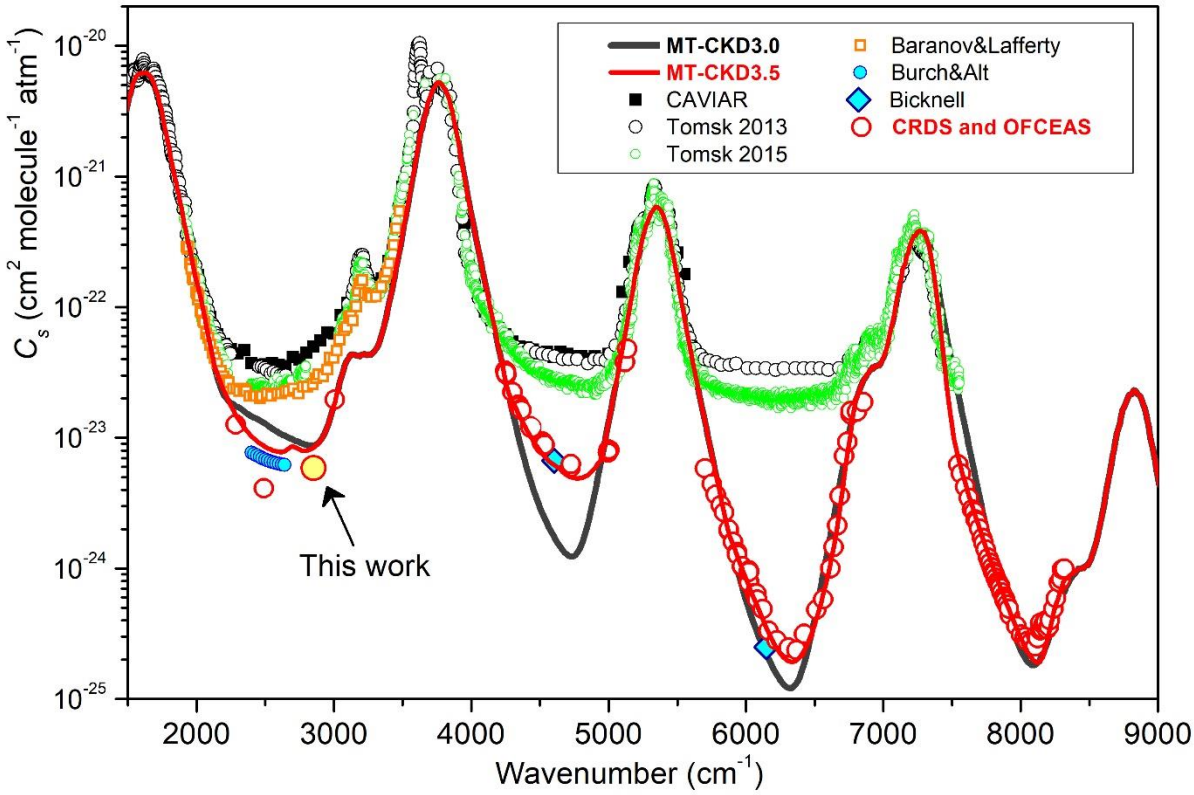

Figure 8: *Overview comparison of the self-continuum cross-section of water vapor near room temperature between 1500 and 9000 cm^{-1}.*
Solid lines show different versions of the MT_CKD V3.0 and V3.5 versions at 296 K [2-4]. Experimental results were obtained by OFCEAS and CRDS (red circles; Campargue et al. [13], Richard et al. [14], Lechevallier et al. [15], Ventrillard et al. [18], Mondelain et al. [16], Vasilchenko et al. [17] and this work); by FTS from Baranov and Lafferty [29]) (light green circles), from CAVIAR consortium (black squares; Ptashnik et al. [8]), from Tomsk2013 (orange circles; Ptashnik et al. [9]), from Tomsk2015 (green circles; Ptashnik et al, [10]), with a grating spectrograph by Burch and Alt [5,6] (dark blue circles) and by interferometric calorimetry (blue diamond; Bicknell et al. [32]).

The present measurements of the self-continuum cross-section of water vapor at 2853 cm^{-1} and of the foreign-continuum cross-sections at 4302 cm^{-1} complete the previous CEAS characterizations of the water vapor continuum absorption that we performed in the 4.0, 2.1, 1.6 and 1.25 µm windows. **Figs. 8** and **9** present an updated overview comparison of our measured C_S and C_F values to the MT_CKD model and to previous FTS measurements. The consistency of our measurements performed since 2013 by different experimentators, with two different CEAS techniques (CRDS and CEAS) using a large variety of spectrometers covering very different spectral regions, has to be underlined. It is now admitted

that the FTS self-continuum values reported by the CAVIAR consortium at room temperature are largely overestimated in the windows because they were affected by experimental biases. The current version of the MT_CKD self-continuum has been recently constrained according to most of the CEAS cross-sections in the 4.0, 2.1, 1.6 and 1.25 µm windows. The present C_S measurement at 2853 cm^{-1} together with the previous OFCEAS measurement at the 2490 cm^{-1} spectral point [14], indicate the MT_CKD_V3.5 self-continuum values should be significantly decreased in the center of the 4.0 µm window.

As concerns the foreign continuum, to the best of our knowledge no room temperature measurements were available prior to our OFCEAS and CRDS investigations. The overview comparison of **Fig. 9** indicates that the MT_CKD_V3.5 foreign-continuum is significantly smaller than the observations near the center of the 1.6 and 2.1 µm windows. The two sets of CEAS measurements can be satisfactorily reproduced using a polynomial which is given above for the 2.1 µm window (see caption of Fig. 7) and can be found in Ref. [19] for the 1.6 µm window. The CAVIAR FTS C_F values at 400 K [31] are larger than the room temperature CEAS values. However, the data at disposal do not allow for a conclusive statement about the temperature dependence of the foreign continuum. In the near future, we plan to investigate this issue in more details using a newly developed CRDS cell allowing for measurements over a wider temperature range than allowed by our OFCEAS spectrometers.

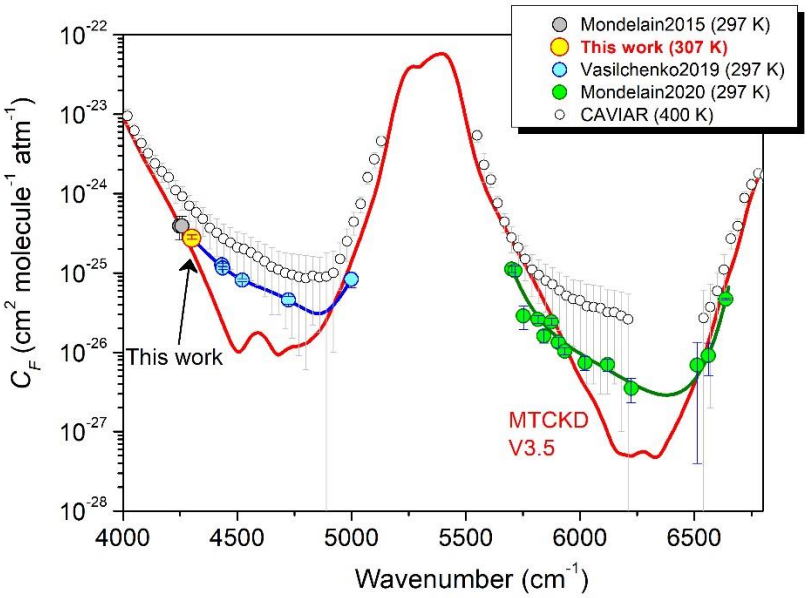

Figure 9. *Overview of the experimental foreign-continuum cross-sections, C_F, reported in the literature and retrieved in this work (red circle) for the 2.1 and 1.6 µm windows and comparison to the MT_CKD_V3.5 model (red solid line). Previous experimental determinations are the CAVIAR FTS values at 400 K from Ref. [31] (black circles), CRDS values (light blue circles) from Vasilchenko et al. [16] at 4250 cm^{-1}, from Mondelain et al. [17] at 4433, 4436, 4522, 4724, 4999 cm^{-1} and from Mondelain et al. [19] in the 1.6 µm window.*

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