

# Measurement and temperature dependence of the water vapor self-continuum between 70 and 700 cm<sup>-1</sup>

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## ABSTRACT

We present new measurements and analysis of the water absorption spectra in the region of the rotational band, between 70 and 700 cm<sup>-1</sup>. The higher pressures of the recordings (up to 16 mbar) as compared to our previous measurements allowed us to extend the retrieval of the water vapor self-continuum absorption from 500 to 700 cm<sup>-1</sup> and to test our earlier results up to 500 cm<sup>-1</sup>. As a result, the continuum amplitude at high wavenumbers, determined with smaller uncertainty, shows an improved agreement with literature experimental data. The measurements were performed at two temperatures (296 and 326 K) using two radiation sources of significantly different power ranges: SOLEIL synchrotron and globar. The quadratic pressure dependence of the self-continuum absorption was verified leading to consistent values of cross-sections derived at various experimental conditions. In addition, we obtained the first data concerning the water vapor self-continuum temperature dependence in the 84–365 cm<sup>-1</sup> spectral range for which we present the preliminary analysis considering the available measurements and theoretical data.

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## 1. Introduction

Understanding the interaction properties of a water molecule with an electromagnetic radiation is of particular interest for climatology, astronomy, and related fields of science. In spite of its small relative concentration in the Earth atmosphere (less than 5%), water vapor is the main absorber of solar radiation (up to 70%) and is responsible for the major part (about 60%) of the greenhouse effect in the thermal infrared radiation. The spectroscopic databases containing pure rotation as well as rotation-vibration transitions of the H<sub>2</sub>O molecule are updated regularly, improving the accuracy of the resonance absorption lines modelling. However, the non-resonant component of the water vapor absorption spectrum, the so-called *continuum absorption* (or just *continuum*), still does not have a generally accepted understanding of its physical origin. In our atmosphere, the water continuum involves two

contributions: the self-continuum due to the interaction of two water molecules, scaling as the square of the water vapor partial pressure, and the foreign-continuum related to the interaction of water molecules with other atmospheric molecules (mainly nitrogen and oxygen), scaling as the product of the water vapor and foreign gas partial pressures. While the expected pressure dependence of the self-continuum absorption has been checked in a number of experimental works (see, for example, the review paper of Ref. [1]), the temperature dependence of the continuum requires extensive investigations. It is generally assumed that the water vapor continuum arises from non-Lorentzian behavior of wings of water monomer lines [2–4] and/or from bimolecular absorption, including a large contribution from water dimers (true bound and quasi-bound double molecules) [5–11] and a smaller contribution from free molecular pairs (two molecules experiencing one-touch collision) [5,6,9,12]. Note that each continuum component has its own temperature dependence.

The continuum amplitude is small compared to the absorption at the center of resonance lines. Nevertheless, its integrated

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contribution to the atmospheric absorption is larger than the contributions from major greenhouse gases as CO<sub>2</sub> and CH<sub>4</sub>. Thus, proper modeling of the continuum is an important part of the Earth radiation budget calculations [1].

The semi-empirical MT\_CKD model (after the names of the authors Mlawer-Tobin-Clough-Kneizys-Davies) of the water vapor self- and foreign-continua is the standard model incorporated in radiative transfer codes [13,14]. Predictive ability of the model for different spectral regions and temperatures and its step by step improvement following new experimental data can be traced for example in Refs. [9,15–19]. Continuum measurements can be performed directly in the atmosphere from the emitted (down-welling) spectral radiance [20,21] or using external radiation source over a long-distance near-surface path [22]. These measurements are quite sensitive because they use very long optical path length, but suffer from uncertainties related to the atmospheric model, from correlation of the self- and foreign-continuum contributions and poorly controlled environmental conditions (see, e.g. Ref. [23] and refs. therein). Validation tests of the MT\_CKD-3.2 self-continuum model in the far infrared (IR) using room temperature laboratory data revealed a significant overestimation [24]. Thus, new data on the continuum in a broader frequency range under accurately controlled thermodynamic conditions are of great importance for testing and refining the model.

The available quantum-chemical calculations of the true bound water dimer spectrum including its temperature dependence [25] were successfully verified in the millimeter and submillimeter wave range [11,24]. These calculations are believed to be valuable to discuss the physical origin of the water vapor continuum in the whole far-IR range. This knowledge about true bound water dimer absorption allows evaluating the contribution to the continuum from other mechanisms, namely, quasi-bound water dimers and non-Lorentzian wings of monomer lines, which are still poorly known and understood (see e.g. Ref. [4]).

Analysis of the measured continuum temperature dependence may give valuable insights on the different continuum contributions, which have different temperature dependence. Previous experimental investigations of the continuum temperature dependence in the water vapor rotational band were limited to the high and low frequency wings of the band. Temperature dependence within eight transparency micro-windows from 22.5 to 84 cm<sup>-1</sup> was obtained in Ref. [26]. In addition to these measurements, a number of microwave (MW) studies provided data in the range from 3.5 to 11.7 cm<sup>-1</sup> [22,27–32]. Finally the water vapor continuum within the 365–800 cm<sup>-1</sup> range was investigated at room and elevated temperatures (up to 430 K) in Ref. [33], allowing us to estimate the temperature dependence from these data.

This work is a continuation of our previous study dedicated to the measurement and analysis of the water vapor self-continuum absorption in the range of pure rotational H<sub>2</sub>O band (17–500 cm<sup>-1</sup>) [24], in particular, its high-frequency wing (400–700 cm<sup>-1</sup>). In section 2 we present the experimental details used to collect the data of this work. In section 3, we report the improved accuracy on the quantification of the continuum absorption achieved at high wavenumbers as well as its temperature dependence. In section 4, we discuss the obtained temperature dependence in

relation with experimental and theoretical results available in the literature.

## 2. Experiment

The absorption spectra of pure water vapor were recorded using a Fourier Transform Spectrometer (Bruker, IFS-125) equipped with a 260-liters multipass White-type gas cell with 151.75 m absorption pathlength. Spectra were recorded on the AILES beamline of the SOLEIL synchrotron facility [34], using both the synchrotron (in standard operation mode) and a globar as far-IR radiation sources. The measurement method was the same as adopted in Ref. [24]. Three series of spectra were recorded at pressures ranging between 4 and 16 mbar and at two temperatures (296 and 326 K, see Table 1). Water vapor pressure was measured by two capacitance gauges (Pfeiffer 10 and 100 mbar full range with corresponding accuracy of 0.01 and 0.1 mbar).

The room-temperature recordings with the synchrotron allowed extending the upper limit of the retrieved self-continuum absorption from 500 to 700 cm<sup>-1</sup>. The adopted values of the water vapor pressure (16 mbar instead of 6 mbar used in Ref. [24]) allowed increasing the continuum magnitude by a factor of about 7.

Heating the cell for the high-temperature measurements was carried out using several 60° C silicon rubber heaters wrapped around the cell. Four platinum resistance sensors (PT100) were used for continuous temperature monitoring during the recordings. The gas temperature was measured by a sensor located above the radiation beam in the center of the cell, and three sensors were installed to evaluate the temperature gradient along the cell. Before starting the heating procedure, the cell was filled with helium, which possesses the largest thermo-conductivity among available gases. Spectra recordings were undertaken after about 7 h of heating, when stable thermodynamic conditions were achieved. The average temperature inside the cell was determined to be 326 ± 2 K. The measurements were performed using both SOLEIL synchrotron in standard mode of operation and a globar.

The frequency ranges useable for the continuum retrieval for the three sets of recordings are included in Table 1.

## 3. Continuum retrieval

The baseline was determined as an average between the reference spectra recorded with the cell evacuated before and after the measurements with water vapor. The standard deviation of each reference spectra from the averaged baseline was about 0.5%.

The continuum absorption coefficient,  $\alpha_C(\nu, T, P)$ , was retrieved within selected transparency micro-windows between strong neighboring water monomer lines following the same approach as described in Ref. [24]. Namely, it was obtained as the difference of the absorption coefficient,  $\alpha(\nu, T, P)$ , derived from the measured transmittance, and of the calculated resonance absorption coefficient,  $\alpha_R(\nu, T, P)$ :

$$\alpha_C(\nu, T, P) = \alpha(\nu, T, P) - \alpha_R(\nu, T, P), \quad (1)$$

where  $\nu, T, P$  are frequency, temperature, and pressure, respectively.

The resonance absorption spectra were simulated using the

**Table 1**  
Thermodynamic and technical conditions of the recordings.

Series #	Useable frequency range, cm <sup>-1</sup>	Number of acquisitions	T, K	Pressure, mbar	Number of pressure points	Radiation source	Resolution, cm <sup>-1</sup>
1	70–700	200	296	6–16	6	synchrotron	0.02
2	83–361	200	326	4–6	3	synchrotron	0.02
3	143–414	200	326	6–10	8	globar	0.02

line-by-line method [35] as the sum of lines with parameters taken from the HITRAN2016 database [36]:

$$\alpha_{res}(\nu) = \sum_i S_i \Phi_i(\nu), \quad (2)$$

where  $i$  is the line index,  $S_i$  and  $\Phi_i(\nu)$  are the line intensity and normalized line profile, respectively. The lines of all H<sub>2</sub>O isotopologues involving all vibrational states were taken into account. For the line profile we used the following expression:

$$\Phi(\nu) = \frac{R(\nu)}{\pi} \left( \frac{\Delta\nu_c}{(\nu - \nu_0)^2 + \Delta\nu_c^2} + \frac{\Delta\nu_c}{(\nu + \nu_0)^2 + \Delta\nu_c^2} \right), \quad (3)$$

where  $\nu_0$  is the line center frequency, and  $\Delta\nu_c$  is the collisional width.  $R(\nu)$  is the general expression for the radiation term suggested in Ref. [2]:

$$R(\nu) = \frac{\nu}{\nu_0} \frac{\tanh\left(\frac{h\nu}{2kT}\right)}{\tanh\left(\frac{h\nu_0}{2kT}\right)}, \quad (4)$$

where  $k$  is the Boltzmann constant. The standard far-wing cut-off at 25 cm<sup>-1</sup> from the line center was applied, the far wings of the line below and above the cut-off frequency being excluded and the remaining rectangular absorption (the “plinth”) underneath the modeled line profile being preserved.

The water vapor continuum absorption in pure gas near atmospheric thermodynamic conditions has a pressure squared dependence ([1,2,37–39] and references therein) and a temperature dependence which can be conveniently approximated by a power function of the temperature  $T$  [26–29]:

$$\alpha_c(\nu, T, P) = C_s(\nu) \left( \frac{T_0}{T} \right)^{nP^2} \frac{1}{kT}, \quad (5)$$

where  $C_s$  is the self-continuum cross-section (in cm<sup>2</sup>molecule<sup>-1</sup>atm<sup>-1</sup>) at  $T_0 = 296$  K and  $n$  is the temperature exponent.

The linear dependence of the retrieved continuum *versus* pressure squared was checked (Fig. 1). Careful analysis of the dependence in different micro-windows revealed the presence of a small

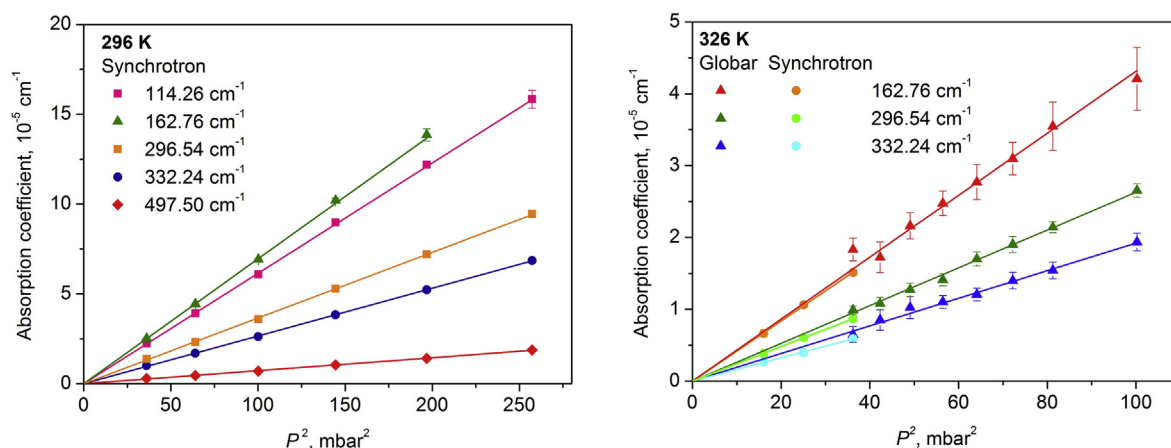
(of the order of one standard deviation of the spectrum noise level) non-zero intercept, smoothly varying with wavenumber, which was assigned to a baseline variation between the water vapor spectra and the reference spectra recorded with empty cell. Obviously, the impact of the baseline drift on the retrieved continuum is more significant at higher wavenumbers, where the continuum magnitude is lower. Neglecting the baseline drift leads to a non-physical sinusoidal modulation of the retrieved continuum spectrum above 450 cm<sup>-1</sup>.

The absorption cross-sections of the self-continuum were determined from the slopes of the linear function  $\alpha_c$  *versus*  $P^2$  fitted to experimental points (see typical examples in Fig. 1). Experimental points perfectly follow the fitted straight lines. This is prominent especially for series corresponding to the synchrotron radiation. Small deviations are noticeable for recordings with the global. This is explained by the significantly smaller signal-to-noise ratio of these recordings as compared to the spectra obtained with the synchrotron which delivers about one order of magnitude more power in the considered spectral range. A good agreement between data retrieved from the 2-nd and 3-rd series of measurements (Table 1) performed at 326 K with different radiation sources is noted (Fig. 1, right panel).

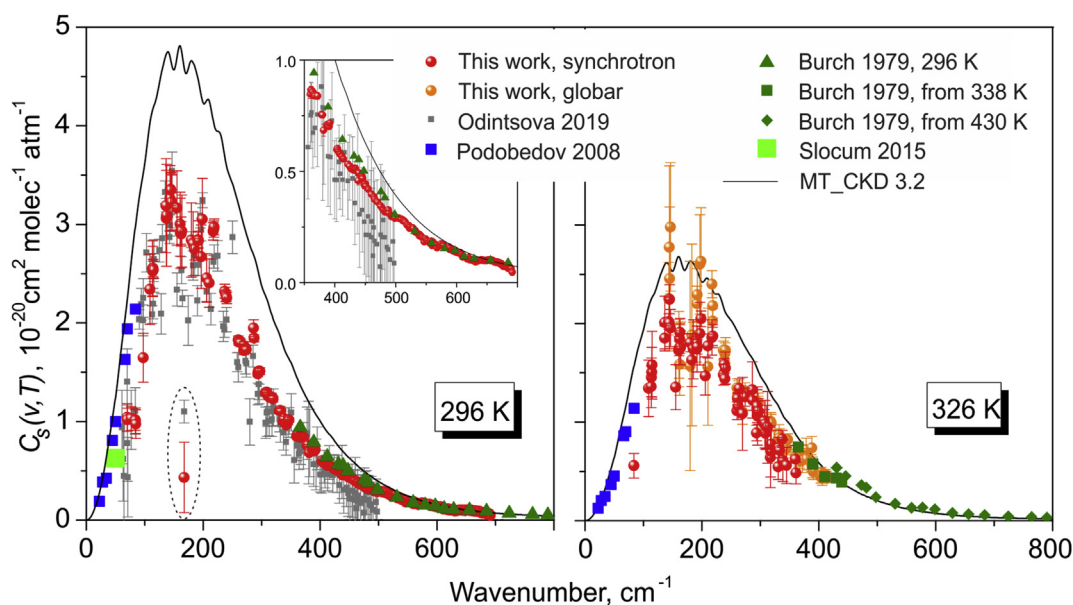
#### 4. Results and discussion

The self-continuum cross-sections retrieved from the three sets of experimental spectra are presented in Fig. 2. As expected, the continuum cross-sections at 326 K are smaller than at 296 K. The plotted uncertainties correspond to one standard deviation of the noisy absorption spectra from its mean value within the current micro-window and uncertainty coming from temperature measurements (the latter is significant only for the measurements at 326 K). The values retrieved from the synchrotron and global spectra agree within their combined uncertainty bars.

In our previous study [24], the water vapor continuum absorption spectrum was recorded up to 500 cm<sup>-1</sup> at room temperature with pressures up to 6 mbar. The coherent (10–35 cm<sup>-1</sup>) and standard (40–500 cm<sup>-1</sup>) radiation modes of the synchrotron were used. These data extended and supplemented previous measurements filling, in particular, the gap between 200 and 365 cm<sup>-1</sup> that had never been studied before. However, the uncertainty of the continuum spectrum within the 350–500 cm<sup>-1</sup> interval was significant. In the current work, higher pressures (up to 16 mbar) were



**Fig. 1.** Continuum absorption coefficient *versus* pressure squared in some micro-windows after the non-zero intercept values (see text for details) were subtracted: *Left panel* – measurements at 296 K carried out with the synchrotron radiation source; *Right panel* – measurements at 326 K performed with the global source and the synchrotron radiation source (triangles and circles, respectively). Error bars correspond to one standard deviation of the noisy signal from its mean value within current micro-window (in some cases error bars are smaller than the size of the symbol).



**Fig. 2.** Cross-sections of the water vapor self-continuum absorption in the region of the rotational band. *Left panel* (296 K): present synchrotron measurements (red circles); Odintsova et al. [24] (grey squares); Podobedov et al. [26] (blue squares); Burch [33] (dark green triangles); Slocum et al. [40] (bright green square). *Right panel* (326 K): present synchrotron and global measurements (red and orange circles, respectively); Podobedov et al. [26] (blue squares), recalculated from measurements of Burch [33] at 338 K (dark green squares) and at 430 K (dark green rhombs). Note that the errors stated in Refs. [26,40] are smaller than size of the symbols and the uncertainty values were not reported in Ref. [33]. Solid black curves are MT\_CKD-3.2 model [14] with the “plinth” subtracted. Note marked outlier at 167.7 cm<sup>-1</sup>. See text for details.

adopted to improve the accuracy of the continuum retrieval in this region. As a result, the previous [24], and new continuum spectra are generally in a good agreement. The largest differences (up to 25%) observed within the 350–500 cm<sup>-1</sup> region fall within the error-bar range of Ref. [24].

Now let us compare our datasets with literature data, which are also shown in Fig. 2. The results of Podobedov et al. below 84 cm<sup>-1</sup> [26] are significantly higher than both our data and the average value obtained by Slocum at room temperature from an extended series of measurements at 50 cm<sup>-1</sup> [40]. Our present 296 K results show an excellent agreement with Burch’s measurement above 500 cm<sup>-1</sup> [33]. A small deviation of the continuum magnitude decreasing with the wavenumber is nevertheless noted within the 350–500 cm<sup>-1</sup> interval (see insert in the left panel of Fig. 2). Concerning higher temperature measurements, two sets of data from Ref. [33] are available for comparison with our 326 K results in the 365–800 cm<sup>-1</sup> range: (i) measurements at 430 K and 296 K (Figs. 2 and 4 from Refs. [33]), (ii) measurements at 338 K and 296 K (Figs. 2 and 3 from Ref. [33]), which can be interpolated at 326 K using Eq. (5), the temperature exponent  $n$  needed for the interpolation being derived from the logarithm of the ratio of continuum cross-sections reported in Refs. [33]. Both interpolations lead to a good consistency with our data (Fig. 2).

It should be emphasized that comparison with the MT\_CKD model requires a correction. Recall that at the stage of the continuum absorption retrieval (Section 3), the resonance absorption spectrum of water vapor was calculated as the sum of spectral lines contributions with a 25 cm<sup>-1</sup> cut-off from the line center without subtracting the plinth, because the plinth with no doubts belongs to the resonance absorption of monomers. For proper comparison of our experimental data and the MT\_CKD model, we subtracted the cumulative plinth of the H<sub>2</sub>O rotational spectrum from the model spectra. The difference between usual and modified MT\_CKD continuum spectra did not exceed 10%.

One can clearly see in Fig. 2 that the MT\_CKD-3.2 continuum model overestimates the self-continuum both at 296 and 326 K in

most of the band but is in good agreement with the new data at wavenumbers higher than 500 cm<sup>-1</sup> at 296 K and higher than 350 cm<sup>-1</sup> at 326 K. This is probably related to the fact that the original Burch measurements available above 350 cm<sup>-1</sup> were used as constraints to construct the MT\_CKD model.

It is worth mentioning that both, at room and elevated temperatures the self-continuum magnitude at 167.7 cm<sup>-1</sup> appears to be an outlier, also observed previously [24]. This point was excluded from the 326 K dataset because its uncertainty becomes a factor of 5 larger than its magnitude. A careful analysis of parameters of the strong nearby water lines was performed using the HITRAN database [28]. It revealed that the self-broadening parameters of the intense water line ( $J_{Ka,Kc} = 4_{3,2} \leftarrow 3_{2,1}$ , ground vibrational state) centered around 170.4 cm<sup>-1</sup> differs significantly from the line broadening of the same pure rotational transitions within a number of vibrational states ( $\nu_1 \leftarrow 2\nu_2$ ,  $\nu_2 + \nu_3 \leftarrow \nu_3$ ,  $\nu_1 + \nu_2 \leftarrow \nu_1$ , etc.). The database suggests a self-broadening parameter equal to 0.434 cm<sup>-1</sup>/atm for all these transitions and 0.723 cm<sup>-1</sup>/atm for the aforementioned ground state line. This contradicts to the well-known fact that relaxation of rotational states of molecules prevails during molecular collision [41,42] and indicates a possible mistype in the database. Note, that the same inconsistencies persist in several previous versions of the HITRAN database (at least since HITRAN2004) and are also observed for corresponding lines of H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>17</sup>O water isotopologues, thus explaining the appearance of a similar low-lying point in the H<sub>2</sub><sup>18</sup>O self-continuum [24]. The use of 0.434 cm<sup>-1</sup>/atm for the 170.4-cm<sup>-1</sup> line broadening parameter increases the self-continuum magnitude at 167.7 cm<sup>-1</sup> at 296 K up to  $3.15(17) \times 10^{-20}$  cm<sup>2</sup>molec<sup>-1</sup>atm<sup>-1</sup>, which becomes consistent with the neighboring micro-window values (Fig. 2).

Several functional laws were suggested to account for the T-dependence of the water self-continuum (e.g. Ref. [19] and references therein). We adopted here the simplest empirical power law



in  $(T_0/T)^n$  because (i) this dependence was previously validated in the considered temperature range in the microwave [27–29] and far IR [26], (ii) it suits well the results of quantum chemical calculations of water dimer spectrum [25], and (iii) we have only two temperature points. Although approximate, this simple law allows drawing several qualitative conclusions on the physical origin of the continuum in the far IR range.

The temperature exponent  $n$  was derived from the continuum cross-sections at 296 K and 326 K (Eq. (5)) over the wide 83–414  $\text{cm}^{-1}$  range. The review of literature data on the temperature dependence [26–29,33] indicates that our data fill the broad gap between 84  $\text{cm}^{-1}$  [26] and 365  $\text{cm}^{-1}$  [33] where no information was available (Fig. 3). Our data can be well approximated by  $n(\nu) = 7.64(67) - 0.0267(57)\nu + 2.8(11)10^{-5}\nu^2$ .

Fig. 3 presents data on the temperature exponents  $n$  available below 800  $\text{cm}^{-1}$ . The water vapor self-continuum is more sensitive to temperature at low frequency where the continuum decreases as  $(1/T)^n$  with  $n$  larger than 9. Around 300  $\text{cm}^{-1}$ , the temperature exponent decreases to a value of about 2. This strong variation can be qualitatively explained as follows. The water vapor continuum absorption is the sum of bimolecular absorption represented, under thermodynamic conditions close to atmospheric, mostly by water dimers (bound and quasi-bound) and a contribution from non-Lorentzian wings of the monomer lines. All these contributions have different temperature dependences. The temperature dependence of the bound water dimer absorption was calculated in Ref. [25]. In the 0–10  $\text{cm}^{-1}$  range, it is well represented by a power function with temperature exponent equal to 9.67 [25]. This value is close to the temperature exponent of the continuum measured in the microwave (MW) range [27,28,30]. The temperature exponents values at 5.1, 7.1, 7.97 and 11.7  $\text{cm}^{-1}$  from Refs. [29–32] (blue circles in Fig. 3) were determined from fitting Eq. (5) to the continuum cross-sections determined by the same way as for our data (Section 3), using the total absorption values presented in Refs. [29–32] and the line-by-line calculated resonance absorption. Note that the spread of different experimental data in Fig. 3 is determined partly by the fact that the exponent value depends on the temperature range of measurements. For example (see Fig. 19 of Ref. [43] and related discussion therein), the  $n$  values evaluated from the results of Ref. [27] above 300 K are in a good agreement with other laboratory MW data. At the same time, the exponent value obtained from the same dataset but below 300 K is 9.6(6), coinciding with

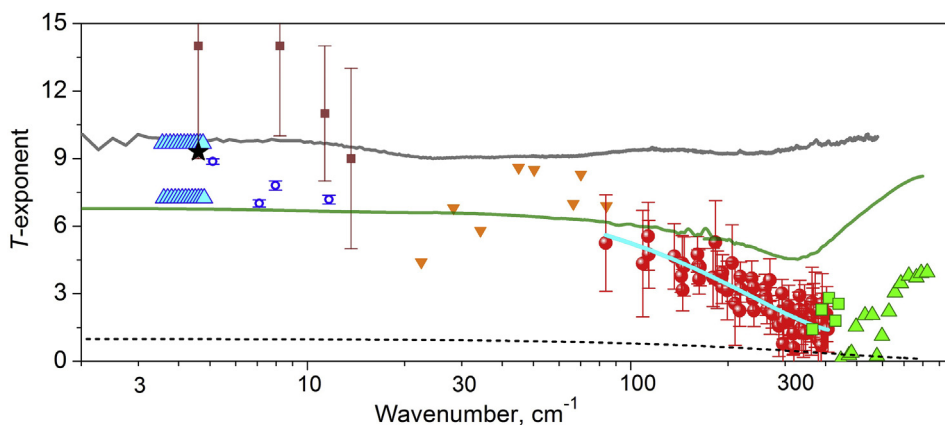
the results of quantum chemical calculations [25]. Thus, being the main source of the water vapor continuum absorption [44], bound water dimers are believed to rule the temperature dependence in the 0–10  $\text{cm}^{-1}$  spectral range.

The temperature exponent decreases with wavenumber, but the calculated value of the exponent  $n$  related to the bound dimers [25] remains almost constant (Fig. 3). The observed frequency dependence of  $n$  indicates that the relative contribution of the bound dimer absorption to the continuum decreases with wavenumber in the considered spectral region. Therefore the contribution of non-Lorentzian wings and quasi-bound dimers seems to become dominant in the close wing of the rotational band near 300–500  $\text{cm}^{-1}$ . Similar behavior was recently observed within the first two vibrational water vapor bands centered at 1600 and 3600  $\text{cm}^{-1}$ , which shows stronger temperature-dependence in the spectral intervals where bound water dimers are expected to be the main contributor and much weaker temperature dependence in the close band wings (see Fig. 4b in Ref. [19]).

At high wavenumbers the temperature exponent tends to increase. We believe that the observed minimum near 500  $\text{cm}^{-1}$  is related to the exponential decay of sub-Lorentzian far wings of monomer lines at large detunings from the line center [4]. Because of this fast decay, the wing's contribution to the continuum is rather well localized within rotational and ro-vibrational bands of the monomer. Meanwhile, the dimer absorption bands are much broader due to multiple strongly coupled thermally populated intermolecular vibrational modes, their combinations and overtones. Therefore, the continuum in transparency windows between monomer bands can be expected to be ruled by dimers. This hypothesis is supported by experimental studies in the IR range (see Fig. 5 and related discussion in Ref. [45]). Thus the observed minimum in  $n(\nu)$  may reveal a change in the dominant contributor to the continuum.

The temperature dependence of the MT\_CKD continuum absorption is not explicitly characterized by a temperature exponent. For comparison purposes, the MT\_CKD exponent was determined using Eq. (5) from the MT\_CKD self-continuum cross sections without the cumulative plinth of the  $\text{H}_2\text{O}$  monomers lines (see details above) at 296 K and 326 K. In the mm spectral range, the MT\_CKD exponent is slightly lower than other data but becomes higher in the far IR.

It should be noted that all data in Fig. 3 include the temperature



**Fig. 3.** Water vapor continuum temperature exponent  $n$  versus wavenumber: present data (red circles) and its approximation (cyan curve) at temperatures of 296 and 326 K, Podobedov et al. [26] at 293–333 K (orange triangles), Koshelev et al. [27] at 270–330 K (bottom cyan triangles) and Tretyakov [43] the same data at 270–300 K (top cyan triangles), Liebe et al. [28] at 282–316 K (black star), data from Lille university [29–32] at 296–346 K (blue circles) and Katkov et al. [22] field measurements at 257–270 K (brown squares), data recalculated from experimental spectra at 296 and 430 K (green triangles) and at 296 and 338 K (green squares) from Burch [33] (see text for details), MT\_CKD-3.2 model [14] at 296 and 326 K (green curve), bound dimer [25] at 257–327 K (grey curve), stimulated absorption term between 296 and 326 K (dash curve). All presented  $n$  values are given in accordance with Eq. (5).

exponent of the term  $(1 - \exp(-h\nu/kT))$  due to stimulated absorption. The temperature exponent of this term is frequency independent both when  $h\nu \ll kT$  (MW range) and  $h\nu \gg kT$  (IR range), but decreases monotonously towards the IR. The impact of this term is general for all absorbers. It contributes to the continuum independently of its origin and does not affect the above discussion about the different continuum absorption mechanisms.

Finally, let us note that available information about the continuum is still insufficient for constructing a complete predictive physically justified model. The development of a general approach for such modeling can be traced in Ref. [4,6,9,43]. However, much more efforts from experimental and theoretical sides are required to achieve this goal.

## 5. Conclusions

Water vapor self-continuum absorption spectra in the region of the rotational band ( $70\text{--}700\text{ cm}^{-1}$ ) have been determined at room (296 K) and elevated (326 K) temperatures with a high vapor pressure (up to 16 mbar). New data on the continuum at 296 K validate and refine results of our earlier work [24] in the  $50\text{--}500\text{ cm}^{-1}$  range and are in agreement with Burch's measurement in the  $365\text{--}800\text{ cm}^{-1}$  range [33]. The 326 K absorption spectra allow for the first study of the temperature dependence of the continuum in the  $84\text{--}365\text{ cm}^{-1}$  range. The temperature dependence in the whole range of water molecule pure rotational band was analyzed considering the present results and a review of the literature data. The derived frequency dependence of the temperature exponent allowed for discussing the different physical mechanisms contributing to the continuum absorption in the range of the water rotational band (or below  $800\text{ cm}^{-1}$ ).

## CRedit authorship contribution statement

**Tatyana A. Odintsova:** Investigation, Formal analysis, Validation, Writing - original draft. **Mikhail Yu. Tretyakov:** Investigation, Conceptualization, Writing - review & editing, Supervision. **Anna A. Simonova:** Formal analysis, Validation, Data curation, Writing - original draft. **Igor V. Ptashnik:** Methodology, Writing - review & editing. **Olivier Pirali:** Investigation, Resources, Writing - review & editing. **Alain Campargue:** Investigation, Conceptualization, Methodology, Writing - review & editing.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2020.128046>.

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