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1 **The atmospheric continuum in the “terahertz gap” (15-700 cm⁻¹): review of experiments**
2 **at SOLEIL synchrotron and modeling**

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13 **Key words:** SOLEIL synchrotron, atmospheric continuum, THz gap, dimer, far wings
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15
16 **Abstract**

17 The results of our recent water vapor related continuum studies in the range of the
18 “terahertz gap” at the AILES beam line of the SOLEIL synchrotron using Fourier transform
19 spectrometer are reviewed and summarized. The continuum of pure water vapor and its
20 mixture with N₂, O₂ and dry air were investigated in the 15 – 700 cm⁻¹ range in conditions
21 close to atmospheric. Analysis of the frequency and temperature dependence of the self-
22 continuum revealed a significant contribution of stable water dimer to the observed
23 absorption, which is not taken into account by the MT_CKD semi-empirical model of the
24 continuum, widely used for atmospheric applications. We propose a physically based
25 approach for the continuum modeling, which accounts explicitly for the contribution of
26 dimers and far wings of monomer resonance lines. We applied the suggested approach for the
27 water vapor self-continuum modeling in the H₂O rotational band and **sustained** it by
28 comparison to the SOLEIL data. The frequency dependence of the relative contributions of
29 far wings, stable and metastable dimers to the self-continuum is evaluated. Prospects for
30 further developments of the atmospheric continuum modeling are given.

31 **1. Introduction**

32 In spite of recent progress, the terahertz frequency range (0.3 – 10 THz or 10 – 300 cm⁻¹)
33 remains poorly studied, mostly due to the lack of available radiation sources and receivers.
34 Due to this reason and its location between the microwave and infrared ranges, it is called the
35 "terahertz gap" (see reviews in [[Sizov_2010](#), [Consolino_2017](#)] and references therein). The
36 THz gap is interesting because it contains absorption spectra of many astrophysical, organic
37 and atmospheric molecules. For example, significant lines of the pure rotational absorption
38 spectrum of water vapor extends to a frequency of about 18 THz (600 cm⁻¹), *i.e.* the main part
39 of the band falls into the THz gap. In addition, the maximum of outgoing heat flux of the
40 Earth falls in the THz range. The development of high-speed wireless communication systems
41 in the THz range requires taking into account atmospheric absorption, mainly due to water
42 vapor. Also, to model accurately the Earth's radiation balance it is necessary to take into
43 account the atmosphere absorption, in particular, water vapor absorption.

44 The absorption of electromagnetic radiation by water vapor – the main greenhouse gas
45 in the Earth's atmosphere – is traditionally subdivided into two components, namely, the
46 *resonance absorption* (the sum of the absorption lines, corresponding to roto-vibrational
47 transitions of water monomers) and the smoothly varying with frequency *continuum*
48 *absorption*, or just the continuum (absorption under the resonance lines). The resonance
49 absorption has been much better characterized both theoretically and experimentally than the
50 continuum. This is due (*i*) to the difficulty to measure accurately weak continuum absorption
51 and (*ii*) to the fact that the continuum is determined as a difference between experimental
52 water vapor absorption and calculated resonance absorption spectrum and, therefore, strongly
53 depends on the line shape model and on the accuracy of its parameters. Compared to the
54 resonance absorption, the relative magnitude of the continuum strongly varies: the continuum
55 can be several orders of magnitude weaker than the resonance absorption near the line center
56 and by one order of magnitude (and even more) stronger in between H₂O lines (the so-called
57 "atmospheric" microwindows). The water vapor continuum has to be accounted for in
58 radiative transfer codes modeling our atmosphere. Currently, a semi-empirical continuum
59 model – the MT_CKD [[MT_CKD](#)] is widely used for atmospheric applications. Our recent
60 experimental studies [[Odintsova_2017](#), [Odintsova_2019](#), [Odintsova_2020](#), [Koroleva_2021](#)]
61 have been motivated by the need to validate the MT_CKD continuum model in the THz
62 range. In addition these new data may give new insights on the physical origin of the
63 continuum and serve as the basis for a physically based continuum modeling in a wide range
64 of frequencies and thermodynamic conditions. It is well known that the continuum arises from

65 the collisional interaction of molecules [Vigasin_2003], in particular, *pair interactions*
66 because triple effects can be neglected at atmospheric conditions. Thus, the continuum
67 magnitude varies as the product of interacting molecules concentrations (or partial pressures).

68 The atmospheric continuum consists of a dry and a wet component. The *dry continuum*
69 arises mainly from the interaction of nitrogen and oxygen molecules. The *wet continuum* is
70 related to atmospheric water vapor and arises from the interaction of water molecules with
71 each other (*self-continuum*) and with other atmospheric molecules (*foreign-continuum*). Pair
72 interaction of molecules leads to (i) the formation of bimolecular states including metastable
73 (quasibound) and stable (truly bound) dimers and free-pair states (the latter is known to be
74 dominant contributor to the dry continuum [Vigasin_2003, Bissolles_2003,
75 Serov_Balashov_2020] but provides negligible contribution in pure water vapor at usual
76 atmospheric conditions [Vigasin_1991, Leforestier_2010, Tretyakov_2015]) and (ii) the
77 deviation of the far wings of “observed” water lines from theoretical profiles derived in the
78 impact approximation [Ma_Tipping_Leforestier_2008, Elsasser_1938,
79 Serov_Odintsova_2017]. Each continuum component varies smoothly with frequency, which
80 makes complicated to disentangle the two contributions. Two **complementary** hypotheses on
81 the continuum origin, based on the two aforementioned mechanisms have been suggested for
82 a long time. The hypothesis of the dominant role of far wings of water lines is supported by
83 the fact that sophisticated [Tvorogov_Nesmelova_1994, Klimeshina_2015] or semi-empirical
84 [Clough_1989] modification of line profile at large detuning from the line center were able to
85 empirically account for the scarce experimental data at disposal. This approach constitutes the
86 basis of the MT_CKD model [MT_CKD]. However, as demonstrated in
87 [Tretyakov_Serov_2013] and in subsequent study [Serov_Koshelev_2014], spectral features
88 observed in the continuum in the mm-submm wave range (0.1-0.26 THz or 3.5-8.7 cm⁻¹) can
89 be unambiguously attributed to the stable water dimer absorption. Moreover, quantitative
90 evaluation of the dimer absorption led to the conclusion that this mechanism is dominant in
91 water vapor continuum in this spectral range. Evidence of stable water dimer absorption
92 within H₂O fundamental vibrational bands was also demonstrated [Ptashnik_2011,
93 Birk_2020]. It should be mentioned that different continuum constituents are expected to have
94 different temperature dependence [Vigasin_1991] which could help to discriminate them.
95 These facts form the general theoretical ground for the analysis of the continuum
96 composition.

97 The THz range is very attractive for studying the continuum, mainly because the results
98 of global sophisticated *ab initio* calculations of the bound water dimer spectrum are available

99 in this region [[Scribano_2007](#)]. All possible rotational-vibrational tunneling transitions of the
100 dimer up to its first dissociation limit are explicitly taken into account in these calculations,
101 contrary to the simplified calculations in the IR range (see e.g. [[Kjaergaard_2008](#),
102 [Salmi_2008](#)] and refs therein) which consider the dimer as two individually vibrating
103 monomer units and neglect the low frequency modes involving both molecules (only band
104 centers and band intensities are calculated). The detailed knowledge of the dimer spectrum in
105 the THz range is expected to help to evaluate other physical mechanisms contributing to the
106 measured continuum.

107 For quantitative spectroscopic studies of the continuum absorption in the THz range, a
108 powerful radiation source operating in a broad frequency range is needed. Keeping in mind
109 the characteristic scale of the continuum variation with frequency (hundreds of GHz), the
110 desired operating range of the source should cover tens of THz. The high power, large
111 spectral coverage and high stability of the SOLEIL synchrotron make it an ideal source for
112 this kind of studies.

113 Since 2014, several experimental campaigns have been organized (SOLEIL Projects
114 Nos. 20140227, 20170067 and 20180347), aiming at studying the water vapor continuum in
115 the frequency range of pure rotational water band (about 0.45 – 21 THz or 15 – 700 cm^{-1}).
116 The results of the analysis of the recorded spectra **together with obtained continuum cross-**
117 **sections** have been reported in a series of papers [[Odintsova_2017](#), [Odintsova_2019](#),
118 [Odintsova_2020](#), [Koroleva_2021](#)]. The present contribution summarizes conclusions of these
119 investigations. Furthermore, the approach for physically based continuum modeling is
120 outlined and is applied to the SOLEIL measurements of the self-continuum in the pure
121 rotational water band. This allows making quite definite conclusions about bimolecular
122 absorption and far wings contributions.

123 For the reader's convenience, we briefly recall in the next section, the main
124 characteristics of the measurement method and the experimental conditions, and summarize
125 the obtained experimental data. In the third section, we propose a physically based absorption
126 model, which includes the continuum in a natural way and demonstrate the application of its
127 simplified version to the THz region. In the conclusion, the main results of the trial are
128 presented and prospects for further developments are given.

129
130

131 **2. Experimental data**

132 *2.1 FTS recordings*

133 Spectra were recorded at AILES beamline of SOLEIL synchrotron using a high-
134 resolution Fourier-Transform spectrometer (Bruker IFS-125HR). Coherent radiation (CR)
135 and standard (SR) synchrotron operation modes were used to cover the 15 – 35 cm⁻¹ and 40 –
136 700 cm⁻¹ spectral intervals, respectively. The summary of the various experimental
137 conditions of the recordings is presented in **Table 1**. A multiple reflection cell with effective
138 path length of 151.75 m was used. To record spectra at elevated temperature (326 K), the cell
139 was wrapped with several 60 °C silicon rubber heaters and additional thermal isolation. To
140 evaluate and exclude possible bias due to a change of the base line related to the pressure
141 variation, a two-steps procedure was adopted for the gas mixture. At the first step, the cell was
142 filled with pure water vapor, and then a foreign gas was gradually added. At the second step,
143 the resulting mixture was gradually pumped out. It was assumed that the water vapor pressure
144 is constant during filling and decreases in proportion to the total mixture pressure during
145 pumping out. **The expected water content is generally confirmed by observed integrated**
146 **intensities of unsaturated water lines determined from fitting their shape. It should be**
147 **mentioned, that during the experimental studies no manifestation of the effects of adsorption-**
148 **desorption of water in the cell was observed (that is evidenced by almost instantaneous**
149 **stabilization of water vapor pressure after its injection), which is associated with a very large**
150 **volume of the gas cell compared to its inner surface area.**

151 **Table 1.** Experimental conditions of the various recordings and corresponding reference
152 of their analysis

Sample	Frequency range, cm ⁻¹	Water pressure, mbar	Total pressure mbar	T,K	Resolution, cm ⁻¹	Number of spectra	Ref.
H ₂ ¹⁶ O	15-35	11-16	11-16	296	0.02	2	[Odintsova2017, Odintsova2019]
H ₂ ¹⁸ O	15-35	13-16	13-16	296	0.02	2	[Odintsova2019]
H ₂ ¹⁶ O	40-700	3-16	3-16	296, 326	0.02, 0.002	25	[Odintsova2017, Odintsova2019, Odintsova2020]
H ₂ ¹⁸ O	50-500	2-6	2-6	296	0.02, 0.002	10	[Odintsova2019]
H ₂ ¹⁶ O – air	50-500	4	200-400	296	0.02	9	[Koroleva2021]
H ₂ ¹⁶ O – N ₂	50-500	2-4	20-430	296	0.02	9	[Koroleva2021]
H ₂ ¹⁶ O – O ₂	50-500	4	200-400	296	0.02	9	[Koroleva2021]

153

154 *2.2 Analysis and cross-section retrieval*

155 The experimental transmittance, T , is related to the absorption coefficient, α , through
156 the expression $T = \exp(-\alpha L) \otimes f_{app}$, where L and f_{app} are the absorption pathlength and the

157 apparatus spectral resolution function, respectively. The FTS spectra were analyzed using
 158 commonly accepted approach: the difference between measured (α) and the calculated
 159 resonance (α_R) absorption coefficients is referred to the continuum (α_C):

$$160 \quad \alpha_C(\nu, T, P) = \alpha(\nu, T, P) - \alpha_R(\nu, T, P), \quad (1)$$

161 where ν , P and T are frequency, pressure and temperature, correspondingly. Resonance
 162 absorption was modeled as a line-by-line sum using the HITRAN line list for 6 most abundant
 163 water isotopologues [HITRAN2016] and Van Vleck–Huber line profile [VanWleck_
 164 Huber_1977, Clough_1989]. The standard far-wing cut-off at 25 cm^{-1} from the line center was
 165 applied, the far wings of the line below and above the cut-off frequency being excluded and
 166 the remaining almost rectangular absorption (the “pedestal” or “plinth”) underneath the
 167 modeled line profile being preserved as an intrinsic part of the resonance absorption. Note that
 168 a different choice is made in the MT_CKD model for which the plinth is considered as part of
 169 the continuum. It should be mentioned, that in the sub-THz frequency range ($15 - 35 \text{ cm}^{-1}$),
 170 line shape parameters measured by microwave methods [Golubiatnikov_2006,
 171 Golubiatnikov_2005, Golubiatnikov_2008, Koshelev_2011, Koshelev_2007,
 172 Tretyakov_2013] were used instead of HITRAN values, when available. This allows us to
 173 determine the continuum practically in the whole spectral range recorded contrary to the
 174 majority of previous investigations in this range [Burch_1981, Podobedov_2008] and in the
 175 IR [Burch_1981, Burch_Alt_1984, Ptashnik_Shine_2011, Campargue_Kassi_2016], where it
 176 was determined only in points corresponding to microwindows of transparency due to the
 177 necessity of minimizing the contribution of line parameters uncertainties.

178 The continuum absorption coefficient can be written as the sum of the self- (α_{self}) and
 179 foreign- (α_{for}) continua:

$$180 \quad \alpha_C(\nu, T, P) = \alpha_{self}(\nu, T, P) + \alpha_{for}(\nu, T, P)$$

$$181 \quad = C_s(T)P_{H_2O}^2/k_B T + C_f(T)P_{H_2O}P_{for}/k_B T. \quad (2)$$

182 Here $C_s(T)$ and $C_f(T)$ are the self- and foreign-continuum cross-sections (in $\text{cm}^2\text{molec}^{-1}\text{atm}^{-1}$),
 183 k_B is Boltzmann constant, P_{H_2O} and P_{for} are water vapor and foreign gas partial pressure,
 184 respectively. For pure water vapor, only the first term of equation (2) remains.

185 The expected pressure dependences (Eq.2) of the continuum absorption were
 186 systematically checked confirming the reliability of the measurements (and in particular
 187 **baseline stability**): the continuum of pure water vapor increases quadratically with pressure
 188 (see e.g. Fig.1 of [Odintsova_2020]), the continuum of a mixture of water vapor with foreign
 189 gas was checked to increase linearly with the partial pressure of the added foreign gas (Fig.2

190 of [Koroleva_2021]) and to decrease as the square of the total pressure during the pumping
 191 out of the mixture (Fig.4 of [Koroleva_2021]). In 40 – 700 cm⁻¹ spectral interval $C_s(T)$ and
 192 $C_f(T)$ values were derived from a fit of the pressure dependence obtained at about 200 spectral
 193 points located in microwindows of transparency. Let us note that, although less accurate, the
 194 C_s values retrieved from wet gas mixtures are consistent with the values obtained with pure
 195 water vapor [Koroleva_2021]. The $C_f(T)$ values obtained from the analysis of the data
 196 corresponding to filling and pumping stages are also in good agreement.

197 The air-continuum cross-section of atmospheric water vapor, C_{f-air} , was obtained by two
 198 ways. In the first one, C_{f-air} was retrieved directly from experimental spectra of mixture of
 199 water vapor with dry atmospheric air (see [Koroleva_2021]). In the second one, C_{f-air} was
 200 calculated from C_{f-N_2} and C_{f-O_2} values retrieved from spectra of water vapor with N₂ and O₂.
 201 Considering the dominant role of pair interactions and atmospheric abundances of major
 202 atmospheric gases N₂ (≈ 78%), O₂ (≈ 21%) and Ar (≈ 1%), C_{f-air} can be expressed as:

$$C_{f-air}=0.78C_{f-N_2}+0.21C_{f-O_2}+0.01C_{f-Ar} \quad (4)$$

204 Since contributions of C_{f-O_2} and C_{f-Ar} were found negligible [Koroleva_2021, Bauer_1998],
 205 C_{f-air} reduces to:

$$C_{f-air}=0.78C_{f-N_2} \quad (5)$$

207 The result agrees with the foreign-continuum retrieved from a mixture of H₂O with dry
 208 air [Koroleva2021]. Both, consistency of all experimental data sets with each-other and
 209 expected pressure dependences serve as a tough validation of obtained experimental data.

210

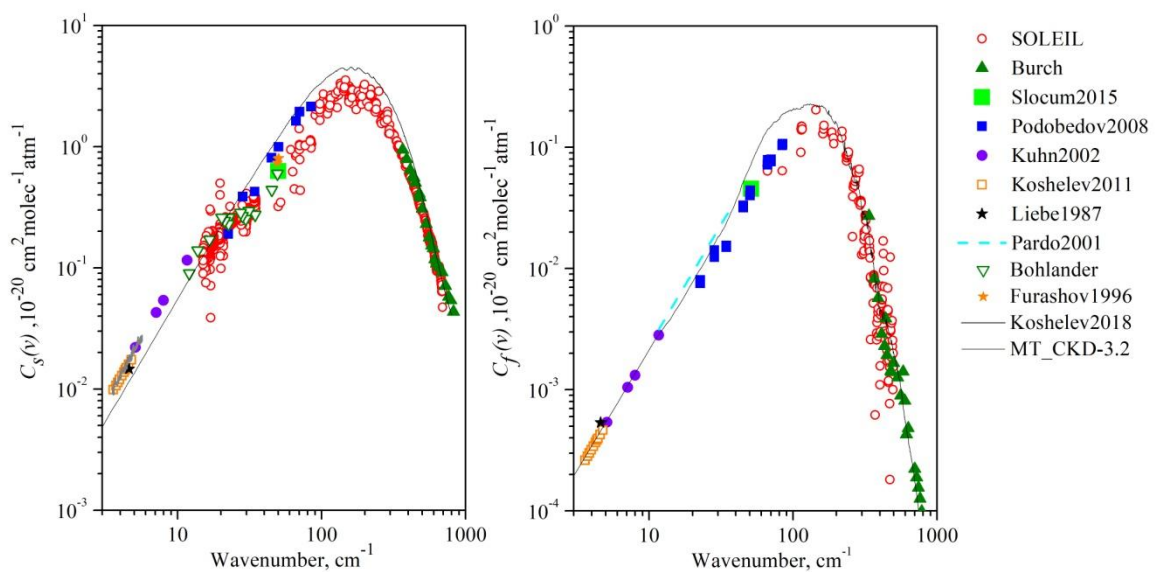


Fig. 1. Self- (left panel) and foreign- (right panel) continuum at 296 K: red circles: SOLEIL measurements [Odintsova_2020,Odintsova_2019, Odintsova_2017, Koroleva_2021], green

triangles: [Burch_1981, Burch_Alt_1984], blue squares: [Podobedov_2008], black star: [Liebe_1987], green empty triangles: measurements of R.A. Bohlander [Burch_1981], light green square: [Slocum_2015], violet circles: [Kuhn_2002], orange empty squares: [Koshelev_2011], orange star: [Furashov_1996], grey curve: [Koshelev_2018], blue dash curve: [Pardo_2001], black curve: MT_CKD-3.2 model [MT_CKD].

211

212 Temperature dependence of continuum cross-section $C(T)$ is empirically approximated
213 using power law [Koshelev_Serov_2011, Liebe_1897, Kuhn_2002]:

$$214 \quad C_{s,f}(T) = C_{s,f}(T_0) \cdot (T_0/T)^n, \quad (6)$$

215 where $T_0 = 296$ K, and n is the temperature exponent. The temperature exponent n of the self-
216 continuum was estimated from C_s at 296 K and 326 K [Odintsova_2020]. Since the
217 temperature difference of the SOLEIL recordings was limited to 30 K, the above empirical
218 law with one adjustable parameter was chosen instead of more complex functions (see, for
219 example, [Ptashnik_2019], [Vigasin_2000]).

220 **Figure 1** presents an overview comparison of the water vapor self- and foreign-continua
221 measurements available in the literature to our data and to the MT_CKD-3.2 model at 296 K.
222 Note that SOLEIL C_s values with estimated uncertainty higher than 15 % are not shown in
223 **Figure 1**, the exception is low-frequency wing of the band ($15\text{-}100\text{ cm}^{-1}$), for which all
224 available values are given (even with uncertainty higher than 50 %). SOLEIL data and their
225 uncertainties are given in Supplementary Materials of our previous papers [Odintsova_2019,
226 Odintsova_2020, Koroleva_2020]. We would like to point out that the spread of experimental
227 points, which is seen in Fig. 1, is the best characteristic of their uncertainty, including
228 systematic errors related, in particular, to uncertainty of resonance line parameters because the
229 continuum is expected to be smooth due to its nature. Note that the estimated experimental
230 uncertainty is often smaller than the spread of points. Overall, the SOLEIL results from
231 [Odintsova_2017, Odintsova_2019, Odintsova_2020] and previous data [Podobedov_2008,
232 Burch_1981, Koshelev_Serov_2011, Kuhn_2002, Liebe_1987, Slocum_2015,
233 Furashov_1996] cover the whole range of the H_2O pure rotational band (significant lines of
234 the band are spread from 0.7 up to about 600 cm^{-1}). Note that the continuum around the
235 intensity maximum of the H_2O rotational band (which is located around 150 cm^{-1} and
236 coincides with the intensity maximum of the continuum) – from 84 to 350 cm^{-1} – was not
237 investigated earlier. Overall, using a wide variety of experimental conditions (pressure range,
238 gas sample temperature, bolometer filter, synchrotron mode), our successive measurement
239 campaigns at SOLEIL synchrotron allowed us collecting data covering the broad frequency
240 range from 15 up to 700 cm^{-1} (with minor problems at the edges of the studied frequency
241 range related to insufficient radiation power) and estimating the temperature dependence of

242 the self-continuum in the 84– 414 cm^{-1} region [Odintsova_2020]. Data of different campaigns
243 are consistent with each other. Above 350 cm^{-1} , an excellent agreement with Burch's
244 measurement is noted [Burch1981, Burch_Alt_1984]. In the 3.5– 84.1 cm^{-1} low-frequency
245 range, several studies are available [Koshelev_2011, Kuhn_2002, Liebe_1987, Slocum_2015,
246 Furashov_1996, Kwon_2021, Yang_2014, Podobedov_2008, Burch_1981]. Our C_s values in
247 the 15 – 35 cm^{-1} range agree with the results of [Podobedov_2008, Burch_1981]. It is worth
248 mentioning an encouraging agreement with unpublished results obtained by R. A. Bohlander
249 and reported by Burch in 1981 [Burch_1981]. Our comparison does not consider the results
250 reported by [Kwon_2021, Yang_2014] in the 10– 33 cm^{-1} range because these broad-band
251 experimental data were fitted assuming purely quadratic frequency dependence of the
252 continuum absorption, thus only the mean values of $C_s(\nu)$ and $C_f(\nu)$ were determined for the
253 whole studied range. Some deviations of our self-continuum from literature data are observed
254 in the range of 50.3– 84.1 cm^{-1} , where our $C_s(\nu)$ values are smaller than the values reported in
255 [Podobedov_2008] and [Slocum_2015, Furashov_1996, Burch_1981] by a factor between 1.5
256 and 2. This deviation can be explained by uncertainty of experimental continuum: the
257 uncertainty of SOLEIL's data coming from low signal-to-noise ratio of our spectra at the edge
258 of the working range of SR synchrotron mode, and uncertainty of data of Podobedov
259 [Podobedov2008] and Bohlander [Burch_1981], that is not reported, but can be estimated by
260 spread of available data.

261 For proper comparison of our data with the MT_CKD model, the cumulative plinth of
262 the H_2O rotational spectrum was subtracted from the model prediction (recall aforementioned
263 convention in the calculation of the resonance line contribution). Although the general
264 agreement with the MT_CKD-3.2 model is satisfactory (Fig. 1a), the detailed comparison
265 reveals some deviations. The MT_CKD-3.2 model overestimates the self-continuum by about
266 30% near its maximum. The agreement gradually improves towards the edges of the H_2O
267 band, which is not surprising because experimental results are used for updating the
268 MT_CKD model. However, we note that, the model does not reproduce experimental
269 frequency dependence of C_s in the mm and sub-mm wave range (3.5 – 50 cm^{-1}). At the lower
270 ($< 10 \text{ cm}^{-1}$) and upper ($> 20 \text{ cm}^{-1}$) parts of this spectral range, the model systematically
271 underestimates and overestimates the continuum, respectively.

272 As concerns the foreign-continuum cross-sections determined in the 60–500 cm^{-1} range,
273 they are consistent with previous experimental studies available in the low-
274 [Podobedov_2008, Pardo_2001, Koshelev_2011, Koshelev2018, Liebe_1987, Kuhn_2002,
275 Kwon_2021, Yang_2014, Slocum_2015] and high-frequency [Burch_1981, Burch_Alt

276 [_1984](#)] wing of the H₂O band. Again, the MT_CKD-3.2 model shows a very good agreement
277 below 50 cm⁻¹ and above 200 cm⁻¹, although some overestimate is notable near the maximum
278 of the band (60–200 cm⁻¹) where previous experimental data were absent.

279

280 **3. Some insights on the origin of the water continuum**

281 *3.1. General outline of atmospheric continuum modeling*

282 The semi-empirical MT_CKD model of the water continuum is the **most widely used**
283 model for atmospheric applications [[Alvarado_Payne_2013](#)]. It covers the 0 – 20000 cm⁻¹
284 frequency range and is updated **periodically** as a new reliable empirical data on the continuum
285 become available (see for instance Fig. 8 of [[Lechevallier_2018](#)] for the infrared windows).
286 The model is a *far wings model*. Resonance line wings modifying χ -factors are **tuned to force**
287 **agreement with observations, on the assumption that deviations are due to departures from the**
288 Lorentzian profile. The model does not take into account the absorption related to the
289 collisional formation of pair molecular states (although this contribution, in particular, coming
290 from free pairs and partly from metastable dimers might be partly included in an effective
291 way in the frame of the approach adopted by the model). This might lead to notable
292 differences in the frequency ranges where the contribution of the dimer absorption is
293 significant. Such deviations were demonstrated in some in-band regions corresponding to
294 fundamental intramolecular vibrational modes of stable water dimer and their overtones
295 [[Ptashnik_Shine_2011](#), [Baranov_2011](#), [Simonova_2022](#), [Birk_2020](#)]. **They are also seen in**
296 **the range of pure rotational band of water dimer (below 40 cm⁻¹) in Fig. 4 of**
297 **[[Odintsova_2019](#)] and Fig. 8 of [[Koshelev_2018](#)].**

298 In [[Serov_Odintsova_2017](#)], a general approach for a physical modeling of radiation
299 absorption by atmospheric molecules was proposed. It explicitly takes into account all classes
300 of absorbers that can be collisionally formed in a gas mixture and it does not require the
301 introduction of the uncertain continuum term. We remind below the basic idea of this
302 approach.

303 The traditionally defined continuum can be expressed in terms of the new approach as
304 will be shown below. The general expression for the total absorption coefficient of a mixture
305 of gases is commonly written as:

$$306 \quad \alpha(\nu) = \alpha_1(\nu)\rho_1 + \alpha_2(\nu)\rho_2 + \alpha_3(\nu)\rho_3 + \dots, \quad (7)$$

307 where $\alpha_1(\nu)$, $\alpha_2(\nu)$... are spectra of corresponding species normalized by their densities ρ_1 ,
308 ρ_2 Note that this linear equation is the basis of the traditional approach to the absorption

309 modeling, which neglects the collisional formation of molecular complexes (unaccounted
 310 absorbers) in gases and, therefore, misses the corresponding absorption. The resulting
 311 disagreement with observations leads to necessity of the continuum introduction. To fix the
 312 problem we take into account that monomers of real gas can be in monomolecular,
 313 bimolecular, trimolecular *etc.* states. So the complete exact equation for the total absorption
 314 coefficient in real gas (for clarity let us consider pure gas of identical molecules) looks exactly
 315 the same as Eq. (7) but now $\alpha_1(\nu)$, is the spectrum of monomers (in the units of absorption
 316 coefficient) normalized by number density of monomers or *monomolecular* absorption, $\alpha_2(\nu)$
 317 is similarly the normalized absorption by molecular pairs or *bimolecular* absorption, $\alpha_3(\nu)$ is
 318 similarly trimolecular absorption, and ρ_1, ρ_2, \dots are number densities of corresponding
 319 absorbers. It is obvious that at relatively low pressures when binary collision approximation is
 320 valid, the following relations hold: $\rho_1 = \rho - \rho_2 - \rho_3 - \dots \approx \rho$, $\rho_2 = K_2 \rho^2$ and $\rho_3 = K_3 \rho^3$, where ρ is
 321 the total (including those in multimolecular states) number density of monomers, K_2 and K_3
 322 are equilibrium constants of bimolecular and trimolecular states. Note that the presence of
 323 bimolecular and trimolecular states is taken into account in the virial equation of state of a gas
 324 by the second and the third virial coefficients, which values are related to equilibrium
 325 constants of bimolecular and trimolecular states [Tretyakov_Serov_2011]. Thus Eq. (7) is
 326 written as

$$327 \quad \alpha(\nu) = \alpha_1(\nu)\rho + \alpha_2(\nu)K_2\rho^2 + \alpha_3(\nu)K_3\rho^3 + \dots, \quad (8)$$

328 Note that each contribution (summand of Eq. (8)) may include resonance and non-resonance
 329 components. At the same time, the continuum in accordance with its common definition of
 330 Eq. (1), includes the total contribution of the second, third and subsequent summands and part
 331 of the first summand. Further minor complication of the equation is required for the adequate
 332 comparison between various components of absorption of our and traditional approaches.
 333 Continuum absorption usually characterized by cross-section (absorption coefficient
 334 normalized by product of molecular number density and pressure) in units of $\text{cm}^2 \text{molec}^{-1} \text{atm}^{-1}$.
 335 These units come from resonance absorption modeling for variable quantity of absorbing
 336 molecules which involves integrated line intensity (normalized by molecular number density
 337 in molec/cm^3) and collisional line width (normalized by pressure in atm^{-1}). The total
 338 absorption (in cm^{-1}) can be written as:

$$339 \quad \alpha(\nu) = \rho [\alpha_1(\nu) + \alpha_2(\nu)K_2\rho k_B T + \alpha_3(\nu)K_3\rho^2 (k_B T)^2 + \dots], \quad (9)$$

340 so α_1 and α_2 are in $\text{cm}^2\text{molec}^{-1}$, ρ is in molec/cm^3 , K_2 and K_3 are in atm^{-1} and atm^{-2} ,
 341 respectively. Note that the unit of K_2 is $(\text{molec}/\text{cm}^3)^{-1}$ in Eq.(8), and (atm^{-1}) in Eq. (9). Under
 342 atmospheric conditions the components of the Eq. (9) starting from the third are negligible
 343 [Tretyakov_Serov_2011]. Bimolecular components of the total absorption (Eq. (9)) can be
 344 written as:

$$345 \quad K_2 \alpha_2 = K_{BD}BD + K_{MD}MD + K_F F, \quad K_2 = K_{BD} + K_{MD} + K_F, \quad (10)$$

346 where BD , MD and F (in $\text{cm}^2\text{molec}^{-1}$) are spectra of dimers (stable and metastable) and of free
 347 pairs normalized by their density, K_{BD} , K_{MD} and K_F are stable and metastable dimers and free
 348 pairs equilibrium constants (in atm^{-1}), characterizing their partial pressures (in atm.) as P_X
 349 $= K_X P^2 = K_X (\rho kT)^2$, $X=BD, MD, F$. The approach cannot be fully implemented in the practical
 350 modeling (even within the pair molecular interaction approximation *i.e.* neglecting the third
 351 and all other summands) until sufficient theoretical description is developed for (i)
 352 bimolecular spectra related to major atmospheric constituents *i.e.* of $\text{H}_2\text{O}-\text{H}_2\text{O}$, $\text{H}_2\text{O}-\text{N}_2$, $\text{H}_2\text{O}-$
 353 O_2 , N_2-N_2 , N_2-O_2 , O_2-O_2 , $\text{H}_2\text{O}-\text{Ar}$, *etc.*, including their free pairs and both stable and
 354 metastable dimeric states, and (ii) resonance line shape of monomers at large detuning from
 355 the line center. In this work, we follow this approach but substitute the missing data by
 356 empirical modeling. With these simplifications, we formulate here an alternative to the
 357 MT_CKD approach considering both the contributions of bimolecular absorption and far
 358 wings of monomer resonance lines. The region of the H_2O rotational band is used for
 359 validation tests of the proposed approach.

360 Dry atmospheric continuum component was not considered in the analysis of our
 361 SOLEIL spectra because of its negligible amplitude under the used experimental conditions.
 362 However, we briefly mention its modeling in the considered spectral range just to demonstrate
 363 the relevance of our general approach.

364 Dry continuum is mainly associated with the pair interactions involving N_2 and O_2
 365 molecules. The monomolecular component of the dry continuum, related to the deviation of
 366 the wings of weak resonance lines (quadrupole transitions in N_2 and magnetic-dipole
 367 transitions in O_2) from the Lorentzian profile, can be neglected. Note that in some frequency
 368 intervals a contribution of both mono- and bimolecular absorptions from other minor
 369 atmospheric gas constituents (such as N_2O , CO_2 , CH_4 , *etc.*) may also become notable
 370 [Karman_2019]. In the range of the H_2O rotational band, dry continuum is dominated by the
 371 roto-translational collision-induced bands of N_2 and O_2 pairs. Bimolecular absorption related
 372 to transient dipole in O_2 induced by collisions with O_2 and N_2 is much weaker than
 373 corresponding absorption in N_2 [Boissoles_Boulet_2003], and thus, the O_2 induced dipole

374 related component can be neglected at least at the current stage of continuum modeling, where
375 the uncertainty of much more important contributions is large. The N₂-N₂ and N₂-O₂ collision
376 induced spectra are quite similar to each-other [Boissoles_Boulet_2003]. Thus, the dry
377 atmospheric continuum spectrum can be roughly modeled in the considered range using the
378 scaling function from [Boissoles_Boulet_2003] and N₂-N₂ continuum spectrum. As included
379 in the HITRAN database [Karman_2019], the latter is taken from calculations (including
380 contribution of free pairs, stable and metastable dimers) [Karman_2015, Chistikov_2019],
381 which were recently validated by experiment [Serov_Balashov_2020].

382 As for the wet part of the atmospheric continuum, both self and foreign contributions of
383 bimolecular absorption and the part of monomolecular absorption related to far wings of
384 water resonance lines are significant. It is necessary to take into account three sets of spectra
385 corresponding to all possible pair states of H₂O-A (where A is any atmospheric molecule),
386 including truly bound (stable dimer), quasibound (metastable dimer) and free pairs. The H₂O-
387 H₂O, H₂O-N₂ and H₂O-O₂ pair states are expected to bring the dominant contributions. Most
388 of these spectra have never been calculated. However, according to estimates obtained in
389 [Svishchev_1998, Vaida_2000, Robinson_2003, Kjaergaard_Robinson_2003, Sabu2005,
390 Baranov_2012], the concentration of the H₂O-N₂ and H₂O-O₂ heterodimers in air (about 10
391 ppm near the Earth's surface) is much higher than the concentration of gases, such as CH₄,
392 N₂O, CO and various halocarbons which are of principal importance for the calculation of the
393 greenhouse effect of the Earth's atmosphere. Results of the global rotational-vibrational-
394 tunneling absorption spectrum calculations for H₂O-H₂O stable dimer absorption are available
395 for the 0-600 cm⁻¹ region [Scribano_2007]. This allows us to illustrate the application of our
396 approach to the self-continuum. The approach is detailed below and will be applied in the
397 future to the foreign-continuum and thus to the total atmospheric absorption modeling.

398 3.2. Some specificities of the self-continuum modeling in the range of H₂O rotational 399 band

400 As mentioned above, water vapor self-continuum absorption consists of absorption by
401 molecular pairs (including stable and metastable dimer states and neglecting minor
402 contribution of free pairs [Vigasin1991, Leforestier2010, Tretyakov_Sysoev_2015]) and
403 absorption related to far wings of water resonance lines.

404 The stable water dimer contribution (BD) in the 0 – 600 cm⁻¹ frequency range is taken
405 into account using results of the *ab initio* calculations of its spectrum [Scribano_2007].
406 Results of these calculations were validated by more approximate molecular dynamic

407 approach [Lee_2008] and by experimental observations of the water dimer rotationally
408 resolved spectrum in the 3.5-8.4 cm⁻¹ interval [Tretyakov_Serov_2013,
409 Serov_Koshelev_2014]. Stable dimer equilibrium constant K_{BD} , that is related to its
410 dissociation energy and rules its concentration in water vapor at equilibrium conditions was
411 calculated in [Scribano_2006]. However, the value of K_{BD} retrieved from the experimentally
412 observed rotationally resolved spectrum of the dimer at room temperature
413 [Serov_Koshelev_2014] turned out to be lower by about 35 % (0.036 atm⁻¹, that corresponds
414 to 5×10^{-4} relative fraction of stable water dimers in 16 mbar of water vapor) than the
415 calculated value [Scribano_2006]. This difference is explained [Serov_Koshelev_2014] by
416 the fact, that the equilibrium constant calculations (eq. (10) from [Scribano_2006]) involve an
417 overestimated dissociation energy value (1234 cm⁻¹) in comparison with more recent *ab initio*
418 calculations [Leforestier_Szalewicz_2012] and velocity map imaging method [Rocher-
419 Casterline_2011] (1108 cm⁻¹ and 1105(10) cm⁻¹, respectively). The experimentally retrieved
420 equilibrium constant $K_{BD} = 0.036 \text{ atm}^{-1}$ corresponds to a dissociation energy of 1144(19) cm⁻¹,
421 which is in a reasonable agreement with aforementioned values. This K_{BD} value is adopted in
422 the following modeling.

423 Despite tremendous progress in *ab initio* calculations of bimolecular spectra
424 [Karman_2015], the metastable water dimer (metadimer) absorption spectrum has not been
425 calculated yet because of the very high complexity of this system. Following [Vigasin_2010],
426 we consider two boundary cases to evaluate the spectrum of the water metadimer. In the first
427 extreme case, metastable dimer is a double molecule similar to stable dimer but has a short
428 lifetime. Thus its spectrum is similar to one of stable dimer but homogeneously broadened by
429 the lifetime. Such model was used in [Tretyakov_Serov_2013, Serov_Koshelev_2014]. In the
430 second extreme case, the metadimer is considered as two monomers almost freely rotating
431 near each other, and its absorption spectrum is approximated by the doubled absorption of the
432 monomer also homogeneously broadened due to the short lifetime of the metastable states.
433 This modeling of metastable dimer spectrum was used in [Odintsova_Tretyakov_2013,
434 Ptashnik_Shine_2011, Serov_Odintsova_2017, Simonova_Ptashnik_2020]. The unknown
435 lifetime broadening w is a variable parameter of the model which, in principle, depends on the
436 rovibrational transition. Obviously, neither the first nor the second model can reflect all the
437 characteristics of the metadimer spectrum. For example, in the second one, there will be no
438 characteristic features of the rotation of a pair around its center of mass, and in the first one,
439 the characteristic related to the free rotation of monomers is missing. It is supposed
440 [Vigasin_2010] that metadimer spectrum is intermediate between these two boundary cases

441 and thus can be approximated by a linear superposition of the two boundary cases. This
 442 approximation is expected to be good in the range of pure rotational H₂O band because of
 443 general similarity of extreme case spectra (both have bell-shape and their intensity maxima
 444 coincide).

445 Metadimer equilibrium constant, K_{MD} , can be obtained from the well-established (both
 446 experimentally and theoretically) value of the second virial coefficient, $B(T)$ [Stogryn1959,
 447 Wagner_Pruss_2002, Leforestier_2014, Tretyakov_Serov_2011]:

$$448 \quad B(T) = b_0 - K_{BD}RT - K_{MD}RT, \quad (11)$$

449 where b_0 is the excluded volume, R is universal gas constant. The excluded volume here
 450 represents the part responsible for the free pair states. Empirical approximations of
 451 temperature dependences for $b_0(T)$ and $B(T)$ can be found in [Leforestier_2014] and
 452 [Tretyakov_Serov_2011], respectively.

453 Keeping in mind the used method of the resonance absorption calculation, the
 454 monomolecular component of the total absorption (Eq. (9)) can be written as:

$$455 \quad \alpha_1 = \alpha_R + W \quad (12)$$

456 where W is unknown contribution of an inadequate resonance line shape modeling at large
 457 detuning from the line center. The unaccounted in α_R absorption from far wings of resonance
 458 lines W is taken into account by a simple model suggested in [Serov_Odintsova_2017]. It uses
 459 (similarly to the MT_CKD model) the empirical χ -function modifying Lorentzian wings of
 460 resonance lines:

$$461 \quad \chi(v - v_0) = \left(1 + A \frac{|v-v_0|}{dv_{wing}}\right) \exp\left(-\frac{(v-v_0)^2}{dv_{wing}^2}\right), \quad (13)$$

462 where v_0 is line center frequency, A and dv_{wing} are variable parameters corresponding to the
 463 intermediate wing amplitude and the characteristic width of the wing, respectively. The model
 464 takes into account (i) known facts that real resonance line is ‘‘Lorentzian’’ and ‘‘sub-
 465 Lorentzian’’ in the region of near and far wings, respectively [Clough_1980] and (ii) possible
 466 ‘‘super-Lorentzian’’ behavior in the range of intermediate wings.

467 The continuum absorption cross-section $C_S^{calc}(T)$ (in cm²molec⁻¹atm⁻¹) can be thus
 468 simulated as a sum of contributions of stable and metastable dimer absorption and absorption
 469 from far wings of resonance lines:

$$470 \quad \begin{aligned} C_S^{calc}(T) &= K_{BD}BD(T) + K_{MD}MD(T) + W(T)/P \\ &= K_{BD}D(T) + K_{MD}(kMD_1(T) + (1 - k)MD_2(T)) + W(T)/P, \end{aligned} \quad (14)$$

471 where $MD_1(T)$ and $MD_2(T)$ are spectra of metastable dimer according to the first and the
 472 second aforementioned extreme cases, respectively, and k is the relative fraction of the first

473 model of metastable dimer (MD_1) to the total model of metastable dimer spectrum ($0 \leq k \leq 1$).
 474 To reduce the number of variable parameters, we fix the shape of **the stable dimer** spectrum to
 475 **the calculated one** (spectrum curves from Fig. 10 from [Scribano_2007]) and the equilibrium
 476 constant of stable water dimer to the value listed in **Table 2**. The model of the metastable
 477 dimer absorption spectrum includes **two variable parameters**: the fraction parameter, k , and
 478 the lifetime, w , assumed to be identical for all the transitions. Its equilibrium constant, K_{MD} ,
 479 was fixed to the value found from the second virial coefficient, as follows from Eq. (11) (see
 480 **Table 2**). The far-wing contribution is the most uncertain part and includes two parameters (A
 481 and $d\nu_{\text{wing}}$) which are adjusted to the measurements.

482 The temperature dependence of each continuum component is assumed to follow the
 483 power law (at least for the relatively narrow T -intervals considered in this work):

$$484 \quad X(T) = X(T_0) \left(\frac{T_0}{T} \right)^{n_X}, \quad (15)$$

485 where X refers to BD , MD_1 , MD_2 or W , n_X is temperature exponent.

486 Temperature exponent of the total continuum model is defined as:

$$487 \quad n = \frac{\ln \left(\frac{c_S^{\text{calc}}(T)}{c_S^{\text{calc}}(T_0)} \right)}{\ln(T_0/T)}. \quad (16)$$

488

489

490 3.3. Model validation versus experimental data

491 The model function of the continuum absorption cross-section $c_S^{\text{calc}}(T)$ including its
 492 temperature exponent n was optimized to the experimental data available in the range of H₂O
 493 rotational band (3.5-600 cm⁻¹), **including data from literature** [Podobedov_2008, Burch_1981,
 494 Burch_Alt_1984, Koshelev_Serov_2011, Kuhn_2002, Liebe_1987, Slocum_2015,
 495 Furashov_1996]. We used simultaneous (“multispectrum”) fitting of the model to continuum
 496 cross-sections at 296 K and 326 K and to the continuum temperature exponent n . Final
 497 parameters of the model are summarized in **Table 2**. Note, that a change in A and w with
 498 temperature is expected, since both the relative speed of molecular movement and the internal
 499 energy increase with temperature. The former leads to the interaction time decrease and,
 500 consequently, decrease of possible non-monotonic interaction, which is responsible for the
 501 super-Lorenz behavior of wings [Serov_2017]. The latter decreases the average lifetime of
 502 metadimers. Contribution of the MD_2 component (like bound) of the metastable dimer
 503 spectrum was found to be negligible. This observation supports the choice of

504 [Ptashnik_Shine_2011, Odintsova_Tretyakov_2013, Serov_Odintsova_2017] to model the
 505 metadimer spectrum as a broadened monomer spectrum with double intensity in order to
 506 analyze the in-band infrared continuum. On the other hand, it may indicate that the
 507 experimental K_{BD} value (0.036 atm⁻¹ at 296 K) from [Serov_Koshelev_2014], used in this
 508 work, is somewhat overestimated thus confirming conclusions of the work
 509 [Buryak_Vigasin_2015], where the equilibrium constant for true bound dimers (equals to
 510 0.016 atm⁻¹ at 296 K) was calculated using classical expressions and a complete
 511 multidimensional potential energy surface of interacting monomers.

512

513 **Table 2.** Parameters of the continuum model in the rotational band.

	K_{BD} , atm ⁻¹ [Serov_2014]	K_{MD}^a , atm ⁻¹	w^b , cm ⁻¹	k^c	A^d	$d\nu_{wing}^e$, cm ⁻¹
296 K	0.036	0.016	20	1	19	15
326 K	0.017	0.011	30	1	14	15

514 *Notes*

515 ^{a)} Constrained to the value derived from Eq.(11)

516 ^{b)} Lifetime broadening of metastable dimer spectrum MD_2

517 ^{c)} Relative fraction of the first model of metastable dimer (MD_1) to the total model of metastable dimer
 518 spectrum. Constrained to be identical at 296 K and 326 K

519 ^{d)} Intermediate line wing amplitude

520 ^{e)} Characteristic width of the super-Lorentzian part of the line wing. Constrained to be identical at 296
 521 K and 326 K

522

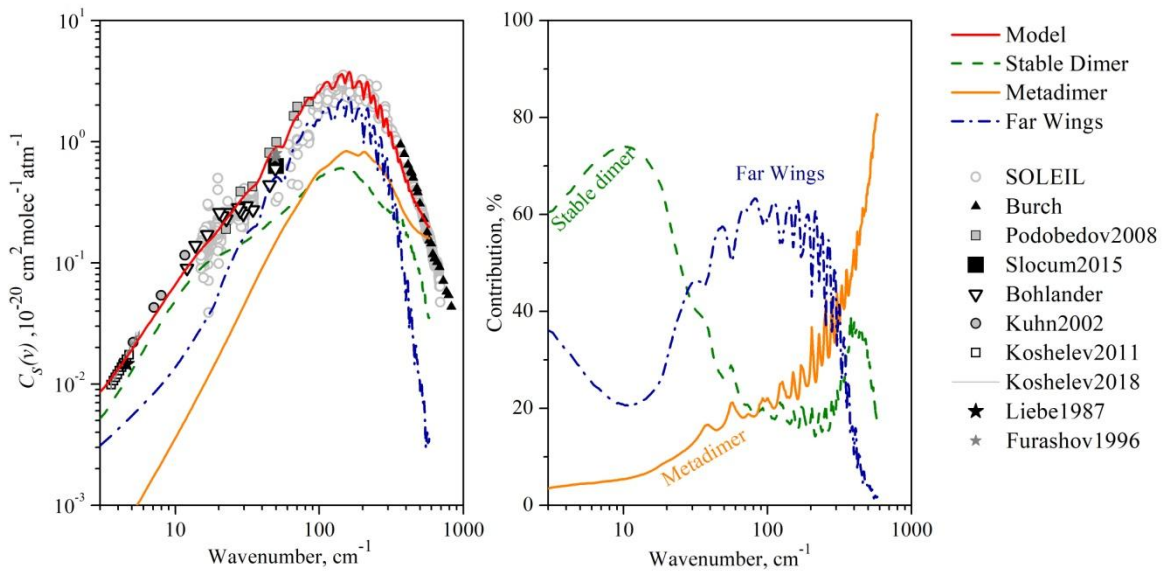


Fig. 2. The self-continuum cross-section (left panel) and relative contribution of continuum components (right panel): grey empty circles: SOLEIL measurements, black triangles: [Burch_1981, Burch_Alt_1984], grey squares: [Podobedov_2008], black star: [Liebe_1987], black empty triangles: measurements of Bohlander [Burch_1981], grey square: [Slocum_2015], grey empty squares: [Koshelev_2011], grey curve: [Koshelev_2018], black circles:

[Kuhn_2002], grey star: [Furashov1996], red solid curve: continuum model, green dash curve: stable dimer model, solid curve: metastable dimer model, blue dash-dot curve: far wings model.

523 **Figure 2** compared the obtained calculated self-continuum at 296 K to the available
 524 experimental data. The various contributions are presented separately in absolute (left-hand)
 525 and relative (right-hand) scales. An overall good agreement is achieved. Note that the
 526 proposed model was constructed in the range up to 600 cm^{-1} , which is limited by the range of
 527 calculated data of the bound dimer spectra [Scribano_2007]. For this reason, the data of
 528 [Burch_1981, Burch_Alt_1984] above 600 cm^{-1} were not taken into account in the analysis
 529 and are shown in **Fig.2** only for comparison. Compared to our measurements, the largest
 530 deviations are observed in the $35 - 84\text{ cm}^{-1}$ interval where the calculated values are
 531 intermediate between our data and those of [Podobedov_2008]. However, the deviation is
 532 within the spread of experimental points.

533 Temperature exponents – n_{MD_1} , n_{MD_2} and n_W – of the revealed continuum components at
 534 experimental temperatures (296 K and 326 K) can be obtained at this step substituting their
 535 modeled spectra (MD_1 , MD_2 and W , respectively) into the following equation:

$$n_X = \frac{\ln\left(\frac{X(T)}{X(T_0)}\right)}{\ln\left(\frac{T_0}{T}\right)}. \quad (17)$$

537 Temperature exponent of stable dimer absorption, n_{BD} , was estimated substituting the
 538 results of *ab initio* calculations (Fig. 10 from [Scribano_2007]) at 268 K and 308 K into
 539 Eq. (17). The temperature exponent of the total continuum in the range of the pure rotational
 540 band is calculated from experimental cross-sections using Eq. (16).

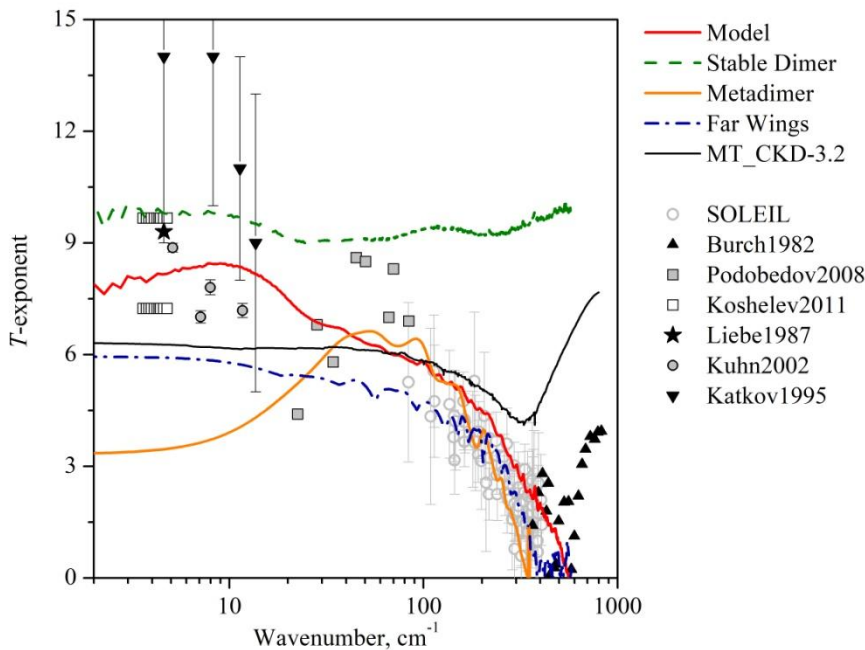


Fig.3. Self-continuum temperature exponent: grey empty circles: SOLEIL measurements, black triangles: [Burch_1981, Burch_Alt_1984], grey squares: [Podobedov_2008], black star: [Liebe_1987], grey empty squares: [Koshelev_2011], black circle: [Kuhn_2002], black triangles: [Katkov_1995], red solid curve: continuum model, green dash curve: stable dimer model, orange solid curve: metastable dimer model MD2, blue dash-dot curve: far wings model, black solid curve: MT_CKD-3.2 model [MT_CKD].

541 The comparison of the experimental and calculated continuum temperature exponents
 542 displayed in **Figure 3** shows an agreement within the spread of experimental points (which is
 543 quite significant). Note that the temperature exponents, n_{BD} , n_{MD1} and n_W are presented
 544 separately. **Temperature exponent frequency dependence of MT_CKD model qualitatively is**
 545 **very similar to the observed one. However the model overestimates experimental values for**
 546 **frequencies higher than 200 cm⁻¹.**

547 It is worth pointing out that the exclusion of any of the three components from the
 548 model significantly worsens the description of the continuum spectrum and its temperature
 549 dependence. For example, excluding the contribution of a stable dimer leads to significant
 550 underestimation of the continuum in the mm-submm range (10 – 40 cm⁻¹) (see Fig. 2, right-
 551 hand). On the other hand, dimer absorption (including stable and metastable states) is
 552 insufficient to describe the continuum within whole range of H₂O pure rotational band. This is
 553 especially true around the band intensity maximum. A similar conclusion was made from
 554 analysis of the in-band continuum in the range of fundamental vibrations
 555 [Serov_Odintsova_2017, Ptashnik_2019]. The exclusion of the metadimer contribution from

556 the model leads to an underestimation of the continuum in the high-frequency wing of the
557 rotational band.

558

559 3.4. The self-continuum contributors

560 Detailed consideration of the continuum in the range of wings and center of the band
561 allowed us to draw some conclusions about its contributors. The mm and sub-mm wave
562 ranges (low frequency wing of the H₂O rotational band) are suitable for the detection of stable
563 dimer spectral signature from spectra recorded at temperatures close to atmospheric.
564 Rotationally resolved water dimer spectrum at close to atmospheric conditions was observed
565 in the 3.5–8.5 cm⁻¹ range using resonator spectrometer [Tretyakov_Serov_2013,
566 Serov_Koshelev_2014]. The observed sequence of rotational peaks consists from a large
567 number of overlapped lines (*E*-type transitions) corresponding to the end over end rotation
568 band of the dimer [Krupnov_Tretyakov_2009]. The sequence is predicted to reach a broad
569 maximum located at room temperature around 20 cm⁻¹, corresponding to the range of the
570 most intense rotational transitions [Scribano_2007]. This maximum is expected to be located
571 on a wide absorption pedestal smoothly increasing with frequency, due to the other rotation-
572 tunneling transitions of stable water dimer in the ground and low energy intermolecular
573 vibrational states populated at room temperature. Moreover, similar smooth frequency
574 dependence of metadimers and absorption related to far wing of resonance lines is expected
575 because these absorptions reach their maximum at much higher frequencies. In order to
576 separate absorption related to stable dimer from other sources, the spectral function of the
577 continuum model, $C_S(\nu)/\nu^2$, is considered in this work. The broad absorption maximum due to
578 the dimer rotational absorption near 20 cm⁻¹ shows up as a characteristic sharp slope of the
579 spectral function (see **Fig. 4**). Series of continuum measurements in the sub-THz frequency
580 range (15 – 35 cm⁻¹) aimed at detecting this spectral signature were performed at SOLEIL
581 [Odintsova_2017, Odintsova_2019] (see Table 1). Frequency dependence of the registered
582 continuum reproduces the spectral signature of the water continuum predicted by *ab initio*
583 calculations [Scribano_2007]. The available experimental data on the continuum spectral
584 function displayed in **Fig. 4** show an overall satisfactory agreement with the model.

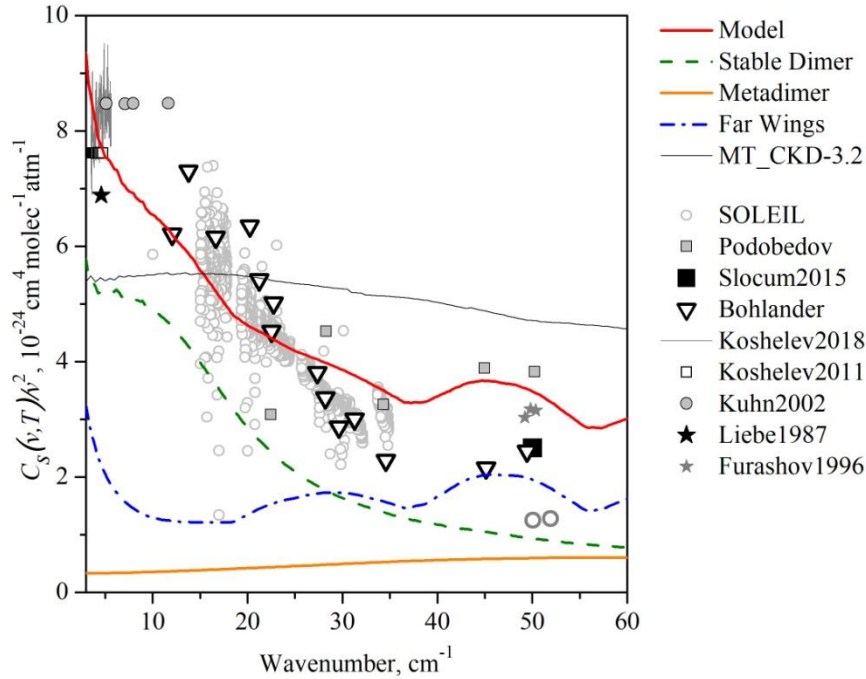


Fig.4. Continuum spectral function: grey empty circles: SOLEIL measurements [Odintsova_2019, Odintsova_2017], black empty triangles: [Burch_1981], grey squares: [Podobedov_2008], grey curve:[Koshelev_2018], grey empty squares: [Koshelev_2011], grey filled circles: [Kuhn_2002], grey star: [Furashov1996], green dash curve: stable dimer model, orange solid curve: metastable dimer model MD_2 , blue dash-dot curve: far wings, red solid curve: resulting continuum model, black thin curve: MT_CKD-3.2 model.

585

586 In the 15 – 35 cm^{-1} range, the relative contribution of the stable dimer absorption to the
 587 continuum is estimated to be about 50 – 75 %. According to our model, relative contributions
 588 of the metadimer absorption and “non-Lorentzian” far wings of resonance water lines are
 589 comparable and significantly lower. Note that the increase of the modeled spectral function of
 590 far wings in the mm wave range ($<5 \text{ cm}^{-1}$) is probably a consequence of the model
 591 approximations and should be taken with caution. The analysis of the temperature dependence
 592 (Fig. 3) in the mm and sub-mm wave ranges indicates that the temperature exponent of the
 593 model (which is within 7 – 8) is very close to that of stable water dimer (about 9 – 10)
 594 [Odintsova_2020]. This confirms that stable dimers bring the dominant contribution in this
 595 range.

596 As illustrated in Fig.2 (right-hand), the contribution of stable dimer absorption to the
 597 continuum decreases to 20 % in the range of band intensity maximum (100 – 300 cm^{-1}), while
 598 the metadimer contribution increases with frequency from 20 to 40 %. The remaining 40 –
 599 60 % is attributed to “non-Lorentzian” far wings of resonance water lines. In the high-
 600 frequency wing (300 – 600 cm^{-1}), metadimer contribution is dominant (40 to 80 % of the total

601 absorption) while stable dimer contribute by about 20 – 35 % and the far wings contribution
602 decreases with frequency from 40 to about 2 %.

603 A similar conclusion is obtained from the temperature dependence (**Fig.3**). The
604 exponent value decreases from 7 – 9 below 50 cm⁻¹ to 2 around 300 cm⁻¹. Modeled values of
605 the exponent n related to metadimers and non-Lorentzian wings demonstrates similar
606 behavior, but calculated values of n related to the stable dimers [[Scribano_2007](#)] remain high
607 and almost constant. The temperature dependence thus confirms that the relative contribution
608 of the bound dimer decreases with wavenumber while the contribution of non-Lorentzian
609 wings and metadimers become significant.

610

611 **4. Discussion and conclusions**

612 SOLEIL's experimental data on water vapor continuum reported in [[Odintsova_2017](#),
613 [Odintsova_2019](#), [Odintsova_2020](#), [Koroleva_2021](#)] have been reviewed and analyzed, that
614 allowed advancing in quantitative characterization and general understanding of the
615 continuum. In particular, the relative contribution of the stable and metastable dimer
616 absorption and far wings of resonance lines has been evaluated in the range of the wings and
617 center of the H₂O rotational band. A physically based modeling of the atmospheric continuum
618 is proposed and tested with the water self-continuum in the 0-600 cm⁻¹ range. The proposed
619 model of the self-continuum, which explicitly takes into account all significant mechanisms,
620 is in a **qualitatively good** agreement with the observed spectra. Semi-empirical description of
621 non-Lorentzian wings of resonance lines and spectrum of metastable pair states are the major
622 uncertainties of this model. A more accurate description of the wings of resonance lines can
623 be achieved, in our opinion, on the basis of semi-classical trajectory based calculations
624 [[Chistikov_2019](#), [Chistikov_2021](#)]. Currently, this method allows calculating bimolecular
625 absorption by non-polar molecules. The extension of the method to molecules possessing a
626 permanent dipole moment will allow the proper calculation of super- and sub-Lorentzian
627 wings of resonance lines. The same approach appears the most promising for approximate
628 calculations of the metadimer spectra until accurate quantum chemical calculations become
629 available. Note that the reproduction of calculations of the bound dimer spectrum either by the
630 trajectory or by quantum chemical method with the use of an improved potential energy
631 surface of the dimer is also much desired, as well as experimental and theoretical verification
632 of the bound dimer equilibrium constant.

633

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