



Water vapor continuum in the range of rotational spectrum of H₂O molecule: New experimental data and their comparative analysis



T.A. Odintsova^{a,*}, M.Yu. Tretyakov^a, O. Pirali^{b,c}, P. Roy^b

^a Institute of Applied Physics, RAS, Uljanova 46, Nizhny Novgorod, Russia

^b SOLEIL Synchrotron, L'orme des Merisiers, Saint-Aubin 91192, Gif-Sur-Yvette, France

^c Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ. Paris-Sud, Université Paris-Saclay, F-91405 Orsay, France

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ABSTRACT

We present laboratory measurements of the water vapor continuum absorption in the far-IR region from 14 to 200 cm⁻¹. These data were obtained using a Fourier Transform spectrometer IFS125 HR associated with a multipass absorption cell and with the synchrotron far-IR broadband radiation extracted by the AILES beamline of SOLEIL facility. The spectra were recorded at room temperature (296 K) and pressures ranging from 2.73 to 15.1 mbar. A comparison with presently available experimental data is presented and the nature of the possible contributors to the continuum is discussed. The new data considerably extend and unify diverging results of previous measurements of the continuum performed in several spots within the range from about 3 cm⁻¹ up to 84 cm⁻¹. The new evidence of significant contribution of the water dimer to the continuum formation is revealed in the range of 14–35 cm⁻¹. Analysis of the possible cause of the observed continuum indicates that its significant part in the range of the maximum intensity of water monomer rotational spectrum cannot be explained within the current understanding of the continuum origin.

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1. Introduction

Water vapor constitutes only about 0.25% of Earth's atmosphere mass [1]. However, it is a major absorber of both incoming solar radiation and reradiated heat. Water vapor absorbs radiation from cm-waves to UV range. In addition to strong resonant lines, water vapor possesses a continuum absorption which varies slowly with frequency, reproducing approximately the resonant absorption bands envelop. In spite of its relative weakness, the continuum contributes significantly to absorption in the atmosphere. This is particularly evident in transparency microwindows, where it can be even

much stronger than the resonant absorption. This has a marked impact on the Earth's radiation balance with consequences for weather forecast and global climate change. It is also important for remote sensing of the Earth and its atmosphere. Experimental studies of the continuum revealed the quadratic pressure dependence as well as the strong negative temperature dependence. Physical mechanism of the atmospheric continuum absorption has been debated during several decades and it is not fully settled yet. In spite of long term history of study, the nature of the continuum has not been established yet even in pure water vapor. It is generally accepted that in the pressure and temperature conditions of the Earth's atmosphere, the continuum is mostly originated from bimolecular absorption, within which it can be approximately separated into contributions of true bound (stable) dimers, quasibound (metastable) dimers and free molecular

* Corresponding author. Tel.: +831 4164866; fax: 831 4363792.

E-mail address: odintsova@ipfran.ru (T.A. Odintsova).

pairs [2]. Far wings of monomer lines also contribute to the continuum, since all actual line shape models were developed within the impact approximation and, therefore, are valid close to the line center frequency. Recent observation of the water dimer rotational spectrum [3,4] in water vapor at atmospheric conditions confirms that essential part of observed continuum in the millimeter wave range can be attributed to water dimer absorption. Extension of this conclusion to other spectral ranges is not straight forward but findings of these studies can serve as a solid base for the continuum origin investigations at higher frequencies.

Investigation of the continuum in the range of $14\text{--}20\text{ cm}^{-1}$ is of particular interest. To date, the most accurate *ab initio* calculations of true bound dimer spectrum [5] predict characteristic absorption feature in this frequency range, which could be separated from the total continuum. According to the calculations, the absorption follows the quadratic versus frequency law up to about $10\text{--}12\text{ cm}^{-1}$. Then it has kind of “hump” with maximum near 15 cm^{-1} followed by further increase of the absorption with smaller rate in the range up to about 100 cm^{-1} . Similar behavior was observed in experimental recordings of water vapor continuum. The continuum was measured by microwave methods in the range of $3\text{--}10\text{ cm}^{-1}$ [6–9], and using FTS in the range of $20\text{--}90\text{ cm}^{-1}$ [10]. Both microwave and FTS studies revealed quadratic frequency dependence in a broad range. However the magnitude of the continuum measured in the $3\text{--}10\text{ cm}^{-1}$ range is larger than one in the $20\text{--}90\text{ cm}^{-1}$ range in about factor of 2. Observation of the hump in intermediate frequency range ($10\text{--}20\text{ cm}^{-1}$) would compromise previous studies and will allow to refine contribution of bound dimer absorption to the continuum. In fact, the hump can be found in the continuum spectrum collected from several studies at the early stage of its investigations (see, e.g., unpublished results obtained by R.A. Bohlander in the range of $15\text{--}50\text{ cm}^{-1}$, which were reported by Burch in 1981–1982s in his compilations of available to date data [11,12]). This experimentally observed deviation from monotonic growth of the continuum absorption was undeservedly forgotten or ignored by the community probably because of the limited number and the large scattering of measurements and their disagreement with more recent data obtained by Podobedov et al. [10]. All known radiation propagation models including the most popular MT_CKD and MPM (see, respectively, [13] and [14] and references therein) describe the continuum by smoothly increasing functions. Thus, additional study of the continuum within $15\text{--}90\text{ cm}^{-1}$ is necessary to refine propagation models and to advance toward understanding of the continuum origin.

In this paper we present experimental study of the water vapor continuum in the frequency range of $14\text{--}200\text{ cm}^{-1}$. This range covers domains, where continuum was not systematically studied before, including one with the water dimer absorption feature predicted in [5]. The calculations of the bound dimer spectrum is available in the range up to 600 cm^{-1} . Experimental data on the continuum together with the *ab initio* calculated spectrum allows to estimate contribution of bound dimer to the continuum in the whole studied range.

2. Experimental details

Water vapor absorption spectra were recorded on the AILES beamline of synchrotron SOLEIL in two frequency ranges: $14\text{--}35\text{ cm}^{-1}$ (coherent synchrotron radiation mode) and $40\text{--}200\text{ cm}^{-1}$ (“classical” incoherent synchrotron radiation mode) using the high-resolution Fourier-transform spectrometer IFS125-HR. To increase the absorbance, water vapor was injected in a multipass White type configuration cell operating at room-temperature ($296 \pm 2\text{ K}$). The total absorption pathlength equals $151.75 \pm 1.5\text{ m}$. It includes 60 passes between mirrors separated by 2.52 m and 0.5 m of space between windows. The zero absorbance spectrum had been recorded with the cell evacuated before the water vapor spectrum was recorded. Repeated recordings of the water spectrum at different pressures served as indirect check of the baseline stability during the experiment.

Keeping in mind very limited synchrotron beamtime allocated to this study, it was necessary to chose optimum experimental conditions, namely resolution, number of coadded interferograms and water vapor pressure.

For the observation of the hump related to bound dimer in the frequency range of $14\text{--}35\text{ cm}^{-1}$ maximum possible sensitivity is important. We limited the spectral resolution to 10^{-2} cm^{-1} to increase the number of averaged interferograms. The water vapor pressure was chosen as a compromise between following considerations. The continuum absorption is in direct proportion to pressure squared. So it achieves its maximum at a pressure of saturated steam (around 28 mbar at room temperature). However, from spectroscopic point of view the recording is informative if optical depth is lower than 10 in most of the recording range. Analysis of resonance line profile is possible in these conditions. It makes more controllable and reliable modeling of the broad band spectrum and allows verifying the sample pressure using known integrated intensities of lines. Moreover, our previous experimental study of the continuum [6] revealed, that at large relative humidity (above 60%, which is about 17 mbar at room temperature) water adsorption on the elements of spectrometer may noticeably affect the result of measurements. Taking all of this into account and examining results of the expected spectrum modeling we decided that the most appropriate water vapor pressure is near 15 mbar . The $14\text{--}35\text{ cm}^{-1}$ spectrum was recorded at 15.1 mbar .

There was one more criterion when the pressure was selected for the continuum measurements in frequency range of $40\text{--}200\text{ cm}^{-1}$. Quadratic dependence of the continuum magnitude on the pressure is the most straightforward consistency check of experimental data, that verifies the baseline stability. For this purpose number of pressures are required. In the current study the spectrum was recorded at two pressures. Value of higher pressure was chosen by analogy with the pressure choice for the $14\text{--}35\text{ cm}^{-1}$ spectrum recording as a compromise between maximum magnitude of the continuum and the possibility of resonant line shape analysis. Both resonant and continuum absorption in this frequency range are stronger than in the range of $14\text{--}35\text{ cm}^{-1}$. So to keep appropriate optical depth the pressure of 5.3 mbar was chosen. Value of lower pressure was chosen smaller by a factor of 2, so the continuum magnitude was expected smaller by a factor of

4. Spectra in this range were recorded with the best possible resolution of the spectrometer because it reduces the number of factors to account for the continuum retrieval.

The experimental conditions used to record the three far-IR spectra are presented in Table 1.

3. Results and discussion

3.1. General approach to the spectra analysis

Total water vapor absorbance A (obtained as $A = \log_{10}(I_0/I)$, where I_0 and I are the signal recorded with empty cell and water vapor respectively), measured in the experiment, was considered as sum of contributions of the resonance spectrum of water monomer A_R and the continuum absorption A_C

$$A(v) = A_R + A_C$$

The absorption coefficient related to resonance spectrum of water monomer was modeled as line by line sum with parameters taken from HITRAN database [15] (for a number of the most intense lines from the 14–35 cm^{-1} range more accurate experimental data on collisional broadening and shifting from works [16–21] were used):

$$\alpha_j(v) = \sum_i S_i^j \cdot \Phi(v),$$

where j is isotopologue-related index, S_i^j – line integrated absorption, $\Phi(v)$ – line shape factor. The Van Vleck–Weisskopf line shape with 25 cm^{-1} far-wing cut-off was used. Following previous experimental studies [6–10] we did not remove the “plinth” under cut line because it belongs to the resonant absorption. For adequate comparison with MT_CKD model [13] the plinth related absorption was calculated (see Supplementary materials) and taken into account.

Table 1

Experimental conditions of spectra recordings.

Frequency, cm^{-1}	T , K	P , mbar	Number of scans	Resolution, cm^{-1}
14–35	296 ± 2	15.1 ± 0.1	1960	0.01
40–200	296 ± 2	2.73 ± 0.01	200	0.00102
40–200	296 ± 2	5.3 ± 0.02	220	0.00102

Strictly speaking the usage of general line profile [22] is more relevant than the Van Vleck–Weisskopf profile, since it is applicable from microwave to infrared and further. It includes the radiation field term, which automatically reduces the line profile to the Lorentz shape in the infrared and to the Van Vleck–Weisskopf shape in the microwave. However, estimations show that relative difference between the Van Vleck–Weisskopf profile and general profile in the whole considered range from 14 to 200 cm^{-1} constitutes less than 1%. So we decided to use the Van Vleck–Weisskopf profile in the present work to keep consistency with previous studies [10,23].

All listed in HITRAN lines up to 225 cm^{-1} of five most abundant water molecule isotopologues were considered. So the total resonant absorbance is:

$$A_R(v) = \sum_j \alpha_j(v) \cdot L,$$

where L is absorption pathlength.

To take into account instrumental line shape of the FTS calculated water monomer transmittance $\left(T_R(v) = 10^{-\frac{A_R(v)}{10}}\right)$ was convolved with functions responsible for finite spectral resolution (“sinc”) and finite field of view (“boxcar”) (see, e.g., [24–26]).

The contribution of the continuum was found as

$$A_C(v) = A(v) - A_R(v).$$

Because of bimolecular nature of the continuum its magnitude should be quadratic function of water vapor pressure P . So the normalized spectrum of the continuum was obtained as

$$K(v) = \frac{A_C(v)}{P^2 \cdot L}.$$

3.2. 14–35 cm^{-1} range

Collisional parameters of all most intense resonance lines in this frequency range are known with high-accuracy from microwave studies [16–21]. This allows us to determine the continuum practically in the whole range of the recording contrary to previous investigations in this range [10–12] and in

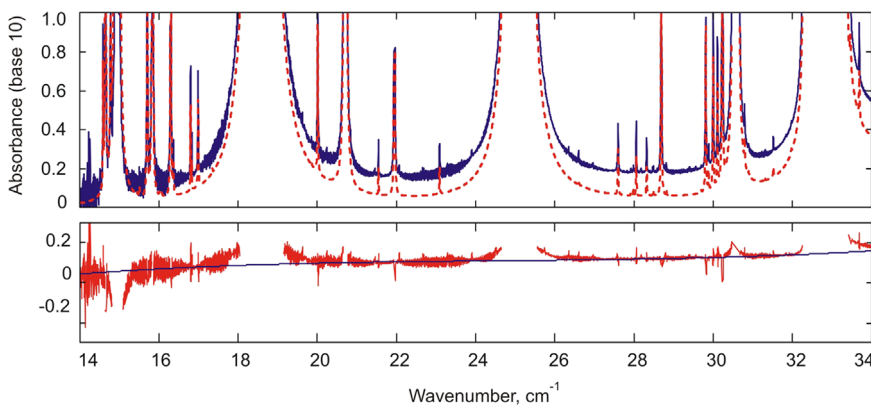


Fig. 1. Upper panel: experimental recording of water vapor absorption spectrum at $T=296$ K, $P=15.1$ mbar (blue trace) and calculated resonance absorption (dashed red trace). Lower panel: retrieved continuum (red trace) and the third order polynomial fitted to the continuum (blue trace).

IR range [27,28], where it was determined in points corresponding to microwindows of water vapor transparency minimizing contribution of resonant lines parameters uncertainties. This gives us an advantage in retrieving underneath strong lines the weak absorption from bound dimer predicted by [5]. Note that the peak should be sitting on the remaining smooth part of the continuum.

Experimental recording of water vapor absorption, calculated water monomer spectrum and retrieved continuum are presented in Fig. 1. A simple quadratic dependence of the continuum absorption with the frequency $\alpha(v) = av^2$, $a > 0$ (as commonly used for the continuum spectrum characterization in mm and far IR ranges [6–8,10,23]) does not fit the

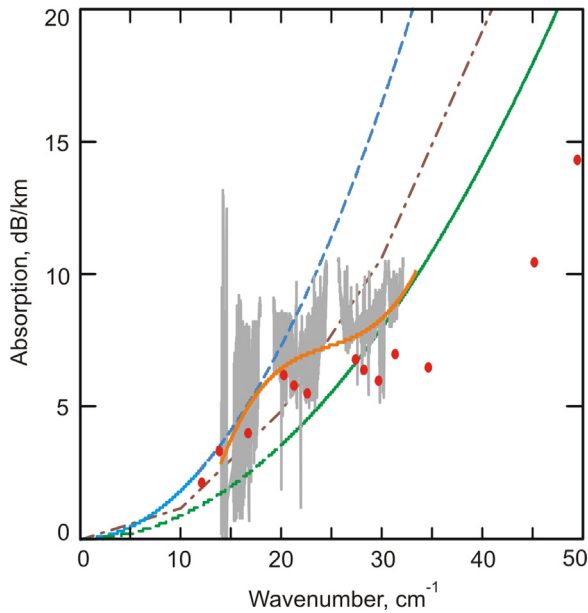


Fig. 2. Comparison of the retrieved continuum with results of previous studies [6–12]. The experimental continuum (gray), its approximation by the third order polynomial (orange), experimentally determined continuum in the millimeter wave range (blue) and its extrapolation (dashed blue), experimentally determined continuum at frequencies 20–90 cm^{-1} (green) and its extrapolation to low frequencies (dashed green), semi empirical model of the continuum MT_CKD 2.5 (dash-dotted brown). Points corresponds to experimental data shown in Fig. 11 from [11].

retrieved continuum. So to better simulate the spectrum, we used a third order polynomial expression $\alpha(v) = a_0 + a_1v + a_2v^2 + a_3v^3$. Parameters obtained from the least squares fitting are $a_0 = -0.1503$, $a_1 = 2.1098 \times 10^{-2}$, $a_2 = -8.348 \times 10^{-4}$, $a_3 = 1.1299 \times 10^{-5}$ supplying the absorption in the units of dB/km and v in cm^{-1} . The polynomial is shown in the lower part of Fig. 1 by the smooth curve.

The same continuum is presented in Fig. 2 together with the quadratic functions and their extrapolations corresponding to the previous continuum measurements in the mm range [6–8] and in the far IR range [10]. Our continuum nicely bends, connecting two frequency dependencies corresponding to the continuum observed in microwave [6–8] and in far IR [10] domains. This bending compromises previous measurements eliminating their disagreement. Continuum calculated by semi empirical model MT_CKD 2.5 [13,29], used for remote sensing, does not reproduce the observed dimer feature. The model represents another kind of compromise between two aforementioned experimental continua and goes just in between.

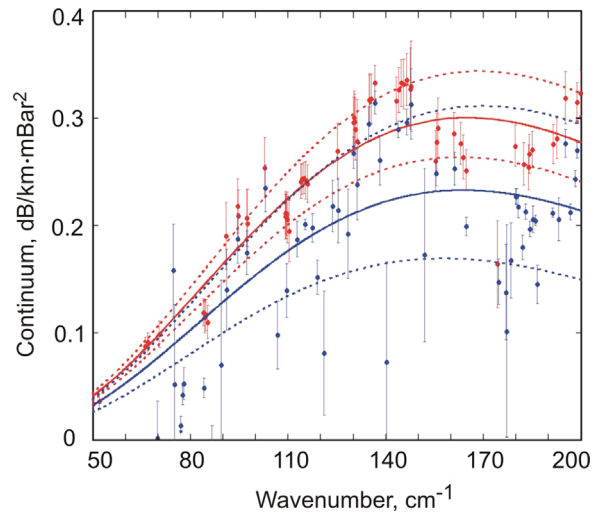


Fig. 4. Continuum retrieved from spectra recorded at 2.73 mbar (blue) and 5.3 mbar (red) in microwindows of transparency within frequency range of 40–200 cm^{-1} (points) and result of their approximation by function (1) (solid lines). Dash lines are 1σ confidence intervals.

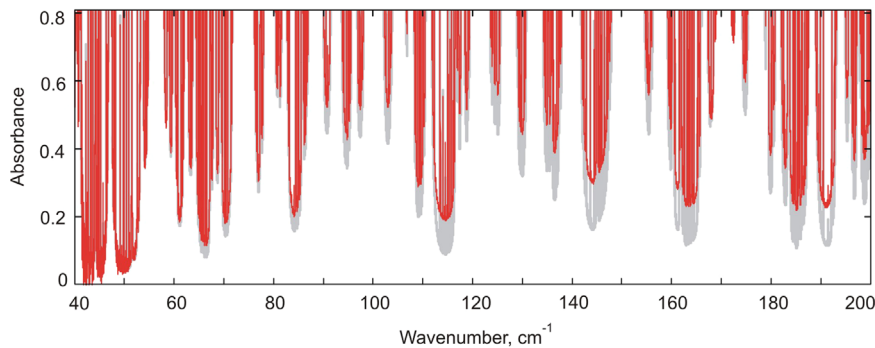


Fig. 3. Experimental recording of water vapor absorption at 5.3 mbar (red) and model spectrum of the monomer resonance absorption (gray).

Our continuum demonstrates very good agreement (Fig. 2) with results of unpublished early measurements performed by R.A. Bohlander [11,12], which is an additional evidence of the reality of the bending observed in our experiment.

Comparison of observed continuum (Fig. 2) and calculated bound dimer absorption (Fig. 13 from [5]) reveals their similarity. The observed continuum bending in combination with its quadratic dependences *versus* frequency at lower and higher frequencies really reminds a “hump” having a broad maximum at about 17 cm^{-1} . Its shape and position are similar to the broad hump predicted by *ab initio* calculations [5]. It should be mentioned that similar peak in the bound water dimer spectrum located in the vicinity of $15\text{--}18\text{ cm}^{-1}$ was also predicted in earlier calculations [30] and [31] based on a simplified model of the dimer. The position of the peak perfectly corresponds to the area where one would expect to find the maximum intensity of rotational spectrum of a prolate top molecule having rotational constant $2B \sim 12.3\text{ GHz}$ as found for water dimer [32]. Observed hump is somewhat broader than predicted one from *ab initio* calculations. We suppose that the most probable reason of the difference is the symmetric top approximation used in the calculation [5]. Total magnitude of the observed continuum is in factor of about 2 larger than predicted for the true bound dimer absorption [5]. Assuming correctness of the calculations

[5], which is supported by experimental observation of the dimer spectrum in mm-wave range [3,4], we can conclude that the calculated bound dimer absorption [5] can explain only part of the observed continuum. That indicates presence of other mechanisms responsible for the continuum origin in this frequency range. Possible sources of this additional absorption will be discussed in Section 3.4.

3.3. $40\text{--}200\text{ cm}^{-1}$ range

Spectral range of $40\text{--}200\text{ cm}^{-1}$ covers the range of maximum intensity of water molecule rotational spectrum. To the best of our knowledge there are no continuum measurements continuously covering this spectral range. Moreover, no experimental data related to the range of $85\text{--}350\text{ cm}^{-1}$ were reported.

Experimental recording of water vapor absorption at 5.3 mbar, 296 K together with the corresponding water monomer absorption calculated as a line by line sum in the frequency range of $40\text{--}200\text{ cm}^{-1}$ are presented in Fig. 3. The difference between experimental and calculated spectra defines the continuum. It was determined by two ways: (i) at points corresponding to all microwindows of transparency between strong water monomer lines, where optical depth is lower than 0.7 (likewise in previous studies in IR [10,28]), and (ii) in whole frequency range of recordings, by analogy with the range of $14\text{--}35\text{ cm}^{-1}$ of the present work. The following empirical function was used for the obtained continuum approximation:

$$\text{cont}(v) = C \cdot v^4 \cdot \exp\left(\frac{-v}{w}\right), \quad (1)$$

where C and w are variable parameters. It was found that coefficients of function (1) corresponding to both methods of the continuum determination coincide with each other within

Table 2
Obtained values of the water vapor continuum empirical parameters (function (1)) and its 1σ uncertainties.

$C, \text{ dB/km} \cdot \text{mBar}^2 \cdot 10^{-8}$	$w, \text{ cm}^{-1}$	Pressure, mbar
1.775 ± 0.276	40.903 ± 1.513	2.73
2.224 ± 0.138	41.410 ± 0.718	5.30

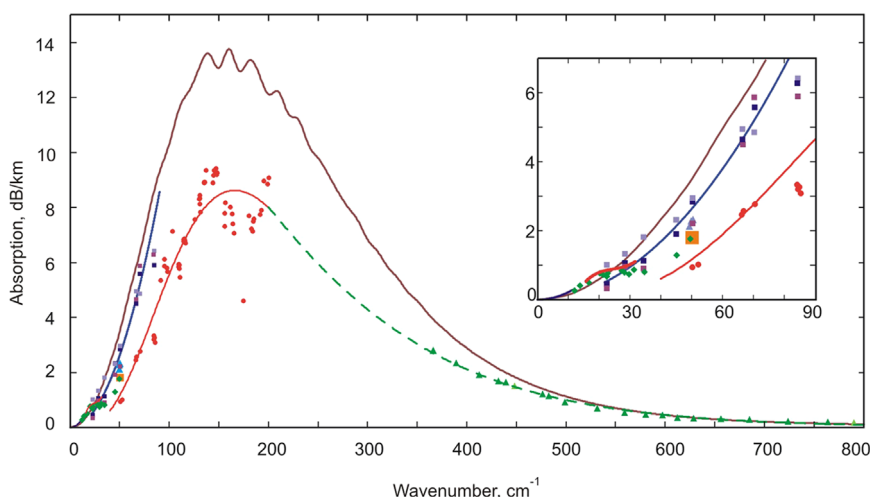


Fig. 5. The retrieved continuum together with previous measurements [6–12,23,33] and MT_CKD model [13]. Our data are presented by red color: circles – continuum in the microwindows of transparency in the range of $40\text{--}200\text{ cm}^{-1}$, solid curve – approximation of the experimental data in the $14\text{--}35\text{ cm}^{-1}$ and $40\text{--}200\text{ cm}^{-1}$ (cut-off 25 cm^{-1}). Blue curve presents approximation of the continuum in the $20\text{--}90\text{ cm}^{-1}$ [10]. Dark blue, bright blue and violet squares – the continuum measured at 293, 313 and 333 K and recalculated to 296 K [10]. Large orange rectangular corresponds to the measurements of [23]. Blue triangles are values from [33]. Green rhombuses correspond to measurements of [11,12] in the range of $15\text{--}50\text{ cm}^{-1}$, green triangles correspond to $360\text{--}800\text{ cm}^{-1}$ data from [11,12], green dash line is their approximation. Brown line corresponds to MT_CKD model [13] (see Supplementary materials for more adequate comparison).

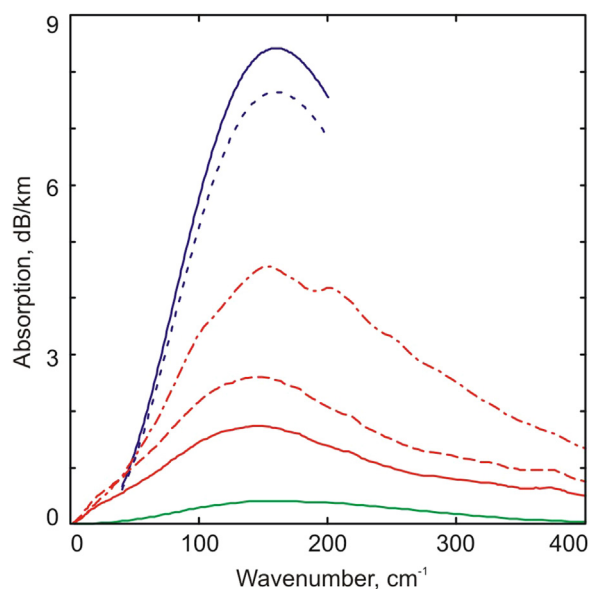


Fig. 6. The continuum constituents. Blue solid and dashed lines correspond to the continuum determined with the 25 and 100 cm^{-1} cut-off of resonant lines, green line – collision induced absorption [41] multiplied by 100, solid red line – bound dimer absorption [5], dashed red line – total dimer absorption (metastable dimer absorption was modeled as lifetime broadened bound dimer absorption), dot-dash red line – total dimer absorption (metastable dimer absorption was modeled as lifetime broadened double monomer absorption).

statistical uncertainty. Approximations of the continuum retrieved from recordings at 2.73 and 5.3 mbar revealed expected quadratic pressure dependence coinciding within 1σ (Fig. 4). Parameters C and w and their statistical uncertainties are presented in Table 2. Parameters obtained from recording at 5.3 mbar are used for our further analysis as more accurate.

The overview of the complete set of information available to date on the water vapor continuum in the range of the rotational band of water molecule is presented in Fig. 5. Very good general coincidence of all experimental data should be noted.

Our data coincide with the measurements of [10] (retrieved in 8 microwindows within frequency range 22.5–84.1 cm^{-1}) within uncertainties of both experiments at frequencies of 22.5, 28.3 and 34.3 cm^{-1} , but differ by about factor of 2 in the range of 45–84.1 cm^{-1} . However, our data in this range are supported by data reported in [11,12]; laboratory investigations made by Furashov et al. [33] and very reliable (resulted from the multispectrum fitting of 145 spectra recorded at different pressures and pathlengths) measurements performed by Slocum et al. [23].

For completeness of the overview of the continuum in the range of water molecule rotational band, the measurements of Burch in the range of 350–800 cm^{-1} [11,12] should be mentioned. Smooth empirical extrapolation of these data (dashed line in Fig. 5) toward the continuum determined in this work demonstrates a good agreement of these two data sets. The MT_CKD model overestimates the continuum in the whole range of water rotational band.

3.4. Discussion

In general, examining possible mechanisms of the continuum formation in gas phase, one can think of two major contributions: monomolecular absorption and bimolecular (related to molecular pairs) absorption. Tri-, four-, etc., molecular absorption can be also considered. Relative number of double, tripple, etc. effects in gas (which is directly related to multimolecular absorption of corresponding order) can be estimated from coefficients of virial equation of the gas state. For water vapor these coefficients can be determined in a broad range of temperatures from very accurate empirical density-versus-pressure data [34]. For the second and third virial coefficients this was done in work [35]. Such evaluation reveals that at usual room conditions (296 K, 60% RH) relative number of pair effects in water vapor reaches 8.8×10^{-4} and tripple – 2.2×10^{-6} . Higher order effects should be even smaller. The estimation shows that for atmospheric conditions we can restrict consideration to monomolecular and bimolecular absorption.

In this work the *monomolecular absorption* is defined as related to one molecule interacting with electromagnetic field from one collision to another. In our opinion, the train of monomolecular oscillations (for the molecular-oscillator approach see, e.g. [36]), which determines the resonance absorption line shape, should include parts where the molecule “feels” the influence of its collisional partner. These parts of the train result in the deviation of the line far wings from the Lorentz profile. They are caused by binary collisional interactions but they are inherent in monomers and lead to the certain resonance line profile. That is why we assign corresponding absorption to monomolecular one. This is contrary to dimeric or collision-induced absorption, which is principally of bimolecular nature (two molecules simultaneously interacting with the field produce one train of oscillations) and is considered here as *bimolecular absorption*.

One can specify two possible sources of the continuum magnitude uncertainty coming from the monomolecular contribution: (i) resonance line shape parameters uncertainty and (ii) unknown far wings absorption. It was discussed in [28] that contribution of the first source to the continuum is very small in fundamental bands. It should be even smaller in the rotational band. The second contribution related to far-wings is more prominent. It was shown in the works of S.A. Clough [37,38] that finite molecular collision time (τ_c) leads to very fast (similar to exponential) decrease of absorption in comparison to impact-approximation line shape models at detuning corresponding to $1/(2\pi\tau_c)$. This resulted in widely accepted convention that line wings follow classical (Lorentzian or Van Vleck–Weisskopf) profile at detuning up to 25 cm^{-1} from line center. At higher detunings the resonance absorption is supposed to be equal to zero. The remaining absorption is automatically attributed to the continuum. Thus, within this convention contribution of far wings to the continuum at each frequency at detuning larger than 25 cm^{-1} is somewhere between Lorentzian and 0, and the corresponding uncertainty of the continuum can be estimated as difference between the continuum retrieved using two resonant absorption models with and without the 25- cm^{-1} cut-off. As was shown in [10], the 100- cm^{-1} cut-off

gives practically the same result as infinite wings. In accordance with these considerations we retrieved the continuum using VVW profile with 25- and 100-cm⁻¹ cut-offs. Results are presented in Fig. 6. They demonstrate that in accordance with the convention, the maximum uncertainty of the continuum due to far wings is less than 10% from the total continuum magnitude.

Let us now consider possible sources of the continuum associated to bimolecular absorption, namely true bound dimers, quasibound dimers and free molecular pairs [39]. It has been accepted that, bimolecular absorption related to free pairs originates from additional transient dipole moment induced by collisions (see e.g. [28] and references therein). Quantitative estimations of possible contribution of this effect to water vapor continuum at conditions under consideration can be made on the basis of results from [40–42], which shows that it is negligible.

The true bound dimer absorption spectrum in the frequency range of 0–600 cm⁻¹ is available from *ab initio* calculations [5]. In the current study qualitative procedure for estimation of the absorption magnitude was applied. It follows from the experiments [3,4,43] that the equilibrium constant of the bound dimer used in [5] and directly related to the absorption magnitude should be reduced by factor of 0.65(6). This factor should be applied in all spectral ranges because it is related only to concentrations of dimers in equilibrium water vapor. Corresponding absorption is shown in Fig. 6 by red solid curve. This evaluation reveals that the bound water dimer absorption can be responsible only for part of the total observed continuum (about 25% in the range of maximum of the monomer rotational band intensity).

To assess contribution of metastable water dimers we considered two rough models corresponding to two extreme cases. These models result from quite natural assumption that absorption cross-section of metastable dimer is between cross-sections of bound dimer and double monomer [44]. Indeed, bound monomers are strongly polarized than free one and additionally the pair acquires its own dipole, which is higher if the state of the dimer is closer to equilibrium. In the first limit the metastable dimer can be considered as two monomers almost freely rotating near each other. Therefore, its absorption spectrum can be calculated as doubled absorption of the monomer broadened by a short lifetime of metastable state. Such model was used in works [28,45]. The lifetime broadening was estimated as 7–20 cm⁻¹ [28]. The second extreme case assumes metastable dimer to be very close to bound dimer, but having short lifetime. So in the second model the metastable dimer has the same spectrum shape as bound dimer but broadened by the lifetime.

Number of metastable dimers or related to this number equilibrium constant K_m can be estimated from well known [39] classical thermodynamic equation:

$$B(T) = B_f + B_m + B_b = b_0(T) - K_m RT - K_b RT,$$

where T – temperature, R – universal gas constant and b_0 is excluded volume. Its value estimated from thermodynamic data as 38.5 cm³/mol [46] was recently confirmed in work [47] on the basis of the most accurate up to date *ab initio* calculated potential energy surface of water dimer. Value of

the bound dimer equilibrium constant K_b calculated in [48] and reduced by the experimentally determined factor of 0.65 (6) [4] was used. Value of the second virial coefficient $B(T)$ was found using its empirical parameterization from [35]. Corresponding to room temperature (296 K) values constitute $K_b = 0.036 \text{ atm}^{-1}$ and $B = -1290.046 \text{ cm}^3/\text{mol}$ resulting in $K_m = 0.018 \text{ atm}^{-1}$.

Two traces related to aforementioned simplified models of metastable dimer absorption summed with the bound dimer absorption are presented in Fig. 6 by red dashed and dot-dashed traces respectively. The first one attains about 35% of the total continuum (in the maximum of the band intensity); meanwhile the second one provides about 60%.

To resume the analysis we can conclude that within commonly accepted convention all known to date continuum originated mechanisms can explain only about 40–65% of the total experimentally observed water vapor continuum absorption at room temperature. Similar treatment of experimental results presented in work [28] indicates that the same problem takes place in the water vapor continuum within the range of fundamental vibrational bands of water monomer [49,50]. In our opinion the main source of the problem is unknown contribution of far wings of resonance lines. Detailed joint analysis of the continuum data within rotational and fundamental vibrational bands devoted to the problem is out of the scope of this paper and will be reported elsewhere.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jqsrt.2016.09.009>.

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