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Millimeter wave continuum absorption in moist nitrogen at temperatures 261–328 K

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ABSTRACT

The paper presents results of extensive experimental study of the water related continuum absorption in a mixture of water vapor and nitrogen in 107–143 GHz frequency range at accurately controlled laboratory conditions. Resonator spectrometer and modified method of measurement that minimizes systematic errors related to water adsorption were employed. It allowed investigation in temperature range 261–328 K, including a first-time laboratory study of the continuum at temperatures below freezing. Coefficients of the common empirical parameterization of the continuum including self (H_2O–H_2O) and foreign (H_2O–N_2) parts are derived and compared with results of the most known previous experimental and theoretical studies demonstrating very good qualitative and in some cases quantitative agreement. Dominating types of intermolecular interactions leading to the observed continuum are discussed.

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1. Introduction

Millimeter wave remote sensing techniques play an important role for studying chemical and physical processes in the Earth's atmosphere as well as for understanding changes caused by anthropogenic activities. Modern instruments and methods of global monitoring of the Earth's atmosphere and underlying surface are sensitive to the accuracy of atmospheric absorption modeling and require accurate information on spectroscopic parameters used. The models describing attenuation of radiation by atmosphere take into account absorption due to resonance or local lines of atmospheric gases as well as non-resonance or continuum absorption. Growing abilities of modern remote sensing techniques put forth unprecedented requirements to the quality of spectroscopic parameters. For example, broadening parameters of the diagnostic atmospheric lines are expected to be

known with an accuracy better than 3% [1,2]; spectroscopic accuracies of 0.2% or better are expected for the ACCURATE mission [3]. Though being relatively weak, the continuum absorption constitutes an essential fraction of the total absorption. In millimeter wave atmospheric windows of transparency its contribution can exceed the contribution of local lines by a factor of ten.

In spite of a long history of the continuum studies its nature is still a matter of discussions. Most consistent approach to the continuum understanding is summarized in the very recent work [4]. Critical review of other existent continuum interpretations is also given in [4]. Within the approach the continuum is considered as bimolecular absorption, which consists of three parts corresponding to different kinds of interacting molecular pairs, namely free monomers, metastable dimers and true bound dimers. Apparently all of the three parts hardly make distinguishable contributions, which are quantitatively different at different meteorological conditions and in different wavelength bands (see, discussions in [4,5] and references therein). To avoid the ambiguity the atmospheric continuum is usually described in applications by three-terms empirical expression (see, e.g. [6,7]), which is

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fitted to the available experimental data. Two of these terms depend quadratically and linearly on water vapor partial pressure, and are called "self-" and "foreign water vapor continuum", respectively. The third term is related to pair collisions of foreign molecules (N_2–N_2, N_2–O_2, O_2–O_2, etc.). It is proportional to the square of the foreign gas partial pressure and is called "dry air continuum".

Experimentally the continuum absorption can be defined as the difference between measured total absorption and contribution from local lines. The latter is usually calculated as line-by-line sum using a uniform line-shape function with corresponding parameters of individual lines, which can be taken from a spectroscopic database (e.g., HITRAN [8]). It should be noted that the definition of the continuum is somewhat arbitrary: it strongly depends on the definition of the local lines absorption. Thus, refinement of spectroscopic parameters in the database may require new derivation of the continuum. Use of different line-shape functions could also significantly affect the continuum [6]. Therefore, any quantitative characterization of the continuum makes sense only for strictly defined contribution of the resonance absorption.

A number of laboratory experimental studies of water-related continuum absorption have been performed in millimeter/submillimeter region (see [6,9–17] and references therein) using either Fabry–Perot resonator or multi-pass cell technique. It was demonstrated in work [18] that results of all of these experiments could contain systematic uncertainty caused by water adsorption on mirrors, windows and coupling elements of the cavity (multipass cell or resonator) used in the spectrometers. Moreover, some systematic discrepancies in obtained results (e.g., in [14,15]) were potentially attributed to water adsorption by authors themselves. Briefly speaking, this effect arises from the principle of the absorption measurement. Spectrometer baseline (background or reference spectrum) is recorded when gas cavity is either empty or filled by dry non-absorbing gas; while for the continuum measurements a moist sample fills the cavity and water molecules can be adsorbed on surfaces of the mirrors, windows and coupling elements. Adsorbed water changes the "dry" baseline that appears as additional absorption in the moist sample. The continuum is the most sensitive part of total absorption in relation to this effect because of its smooth frequency dependence. The effect gets stronger with lowering temperature and increasing humidity of the sample.

To solve the problem, a new approach was proposed [17,18]. The approach is based on variation of the spectrometer optical path-length, which was for the first time implemented in resonator spectrometer in work [19]. Another modification of this method was realized in the new version of the spectrometer [18].

One more motivation of the present work is related to the fact that retrieval of the atmosphere parameters employs nowadays coefficients of the continuum obtained at temperatures, which are higher than usual sea level atmospheric temperature. Although not discussing the usual problems of experimental data extrapolation, we would like to stress that the continuum originating from various constituents of bimolecular absorption may have non uniform temperature dependence.

In the present work we applied the aforementioned method and technique [18] to accurate investigation of the continuum absorption in a mixture of water vapor with nitrogen at ten frequencies ranging from 107 to 143 GHz at atmospheric pressure and temperature varying from −12 to +55 °C. Additional analysis of the results was performed to demonstrate possible contribution of the systematic error due to water adsorption. Comparison of the obtained results with the experimental and theoretical data from most known previous studies was made and can be found in the discussion section of the paper.

2. Experimental details

The continuum absorption in the H_2O–N_2 mixture was investigated using modern version of the BWO based resonator spectrometer, which is described in detail in [18]. Briefly, the gas sample absorption measurement is based on precise determination of the Q-factor of the Fabry–Perot resonator employing fast digital phase-continuous recording of the resonance response and subsequent determination of its width. The spectrometer construction allows eliminating the systematic error caused by water adsorption on the resonator components. The module of two rigidly bounded resonators differing in length by exactly a factor of two is used. Special efforts are undertaken to get identical distribution of electrical field inside both resonators and most identical conditions for water adsorption on both resonator elements. Response widths are measured at the short resonator eigen-frequencies practically coinciding with the ones of the long resonator. The baseline (inherent resonator radiation loss) is measured separately for each resonator filled by dry nitrogen before each experiment.

The sample absorption was measured at ten frequencies: 107.68, 111.97, 115.39, 118.82, 123.11, 127.39, 130.39, 132.53, 137.25 and 143.25 GHz. The module of resonators was located inside the temperature controlled chamber allowing variations from −30 to +60 °C. In the present study the lower temperature limit was −12 °C since its further decrease led to extremely low water amounts in the sample and, consequently, to insufficiently large uncertainties of measured absorption. The sample relative humidity (rh) was varied from 0% to 60% at each temperature. The uniform conditions (temperature and humidity) of the sample inside the chamber (volume is about 180 l) were supplied by fan and controlled by a number of sensors. The temperature was measured within ± 0.5 °C accuracy by eight copper thermistors placed on each mirror and in space nearby each mirror. Two temperature/humidity sensors (Rotronic HygroFlex [http://www.rotronic-humidity.com/]) of ± 0.3 °C/± 1% rh accuracy were placed at the top and bottom of the vertically oriented resonator module. It is worth noting that during each experiment the largest vertical gradients inside the 0.9-meters height chamber did not exceed 1 °C and 1.5% rh for temperature and humidity, respectively. The chamber did not allow variations of the sample pressure so the experiments were carried out at atmospheric pressure. A calibrated pressure meter of 600–800 mmHg range used during the study

supplied the measurement accuracy of total pressure of 0.5 mmHg.

Special attention was paid to the coupling elements, which were found to be the main source of non perfect identity of resonators in our previous study [18]. Small systematic differences in response widths of two geometrically identical resonators of the same length at different humidity and temperature (see Fig. 6 of Ref. [18]) were potentially attributed to detuning of the coupling film angles (about 2°). To decrease influence of the coupling loss on the measured absorption in the present study Polytetrafluoroethylene (PTFE or Teflon) films of 4 μm thickness were utilized instead of previously used less hydrophobic polyethylene terephthalate (PETP) films. Properties of the used films have been partially studied at different values of ambient humidity in work [20]. Film frames in the resonators had the same orientation relative to the initial film sheet and were placed as close as possible at 45° to the cavity axes at the same distance from the lower mirrors. The test measurement of absorption by two identical resonators of the same length was repeated. For the test the second plane mirror was mounted in the middle of the long resonator as in [18]. Results are shown in Fig. 1. The figure demonstrates coincidence of the dependences within the experimental 1σ errors and proves identity of the water adsorption in both resonators.

A measurement cycle at chosen temperature started from the baseline record. The flow of dry nitrogen evaporated from a liquid phase and was permanently blowing through the chamber for dehydration and the temperature inside the chamber was stabilized during the preceding night to achieve the thermal equilibrium. The baseline record was performed when sensors indicated zero humidity and stable temperature. Then, a controlled

amount of water vapor from a flask filled with double distilled liquid water was added stepwise to the nitrogen flow to get at least eight humidity points in the range from 0% to 60% rh. The resonance widths of the resonators were measured at each humidity after the equilibrium conditions were achieved, which usually took about 20 min.

The absorption coefficient $\alpha(v)$ of the sample placed inside cavities was determined at frequency v from the alternately measured response widths of each resonator as [18]

$$\alpha(v) = \frac{2\pi}{c} \left[2(\Delta f2 - \Delta f2_0) - (\Delta f1 - \Delta f1_0) \right], \qquad (1)$$

where $(\Delta f2 - \Delta f2_0)$ and $(\Delta f1 - \Delta f1_0)$ are differences of the response widths of the resonator filled with the studied sample and pure nitrogen for the long and short resonator, respectively.

3. Results

An example of total absorption of radiation by H_2O–N_2 mixture experimentally measured at fixed temperature of 328 K at different frequencies is presented in Fig. 2. It reveals quadratic dependence on water vapor partial pressure P_{H_2O} of the form

$$\alpha = a(T)P_{H_2O} + b(T)P_{H_2O}^2, \qquad (2)$$

where T is the sample temperature. Similar behavior was observed for H_2O–N_2 mixture absorption in earlier experiments in mm-wave transparency windows of atmosphere ([14] and references therein). The term in Eq. (2) responsible for pair collisions of N_2 molecules and proportional to the square of nitrogen partial pressure P_{N_2} is canceled in our experiment because related loss is contained in the sample record as well as in the baseline.
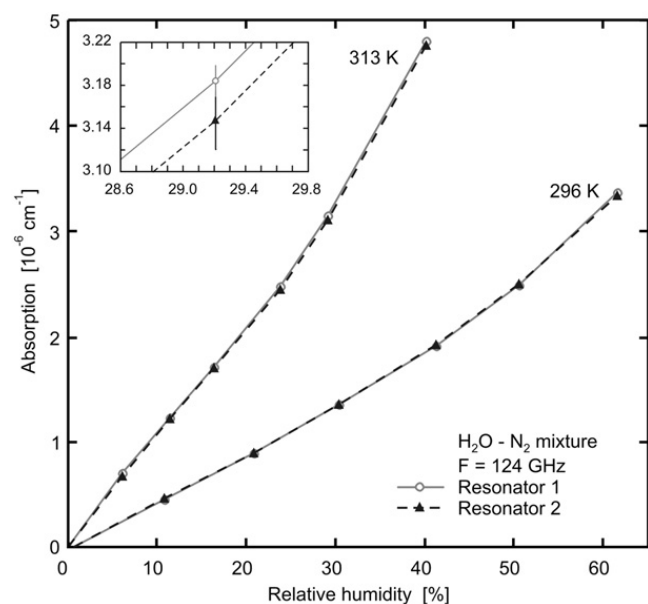

Fig. 1. Absorption coefficient of H_2O–N_2 mixture at 124 GHz measured as a function of relative humidity by two identical resonators of the same length at 296 and 313 K. The zoomed in part of the plot in the vicinity of the point at 29.2% rh and 313 K is shown in the insert. Error bars correspond to 1σ experimental uncertainty.
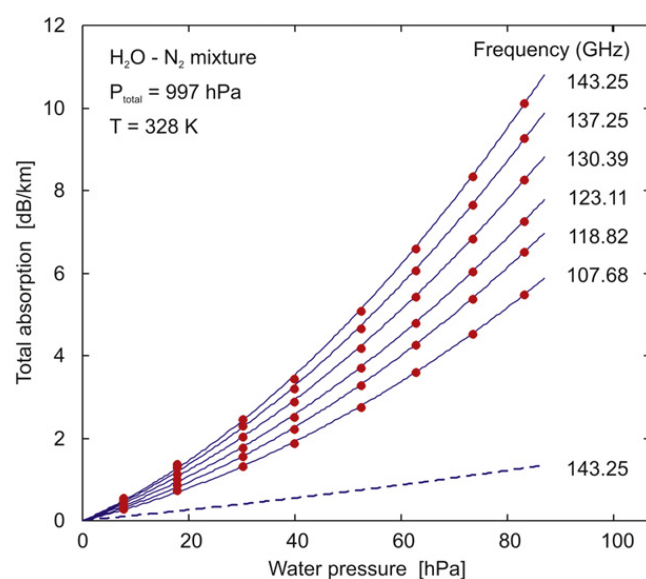

Fig. 2. H_2O–N_2 mixture absorption (circles) measured at different frequencies (shown on the right) as a function of partial water vapor pressure. Total pressure and the mixture temperature are shown on the left. Solid lines represent the result of the fit of Eq. (2) to experimental data. Dashed line is the calculated resonance absorption α_{local} at 143 GHz (see text for details).

Table 1
Results of laboratory measurements of water vapor self- and nitrogen-continuum parameters in mm/submm range. The parameters are in units of dB/km/(GHz hPa)^2. Uncertainties are 1σ statistical errors in terms of the last digits quoted.

Reference	$C_{H_2O}^0 \times 10^{-7}$	n_s	$C_{N_2}^0 \times 10^{-9}$	n_f	Experimental conditions	Line catalog
Present study	0.796(9)	5.24(21)	2.875(35)	0.91(17)	107–143 GHz 261–328 K	R98 [21]
Liebe and Layton 1987 [7]	0.700(20)	7.30(30)	3.362(30)*	0.00(40)	138 GHz 282–316 K	MPM87 [7]
Kuhn et al. 2002 [14]	0.911(16)	5.10(19)	3.002(83)	1.34(28)	153–350 GHz 296–356 K	R98 [21]
Podobedov et al. 2008 [15]	0.400	5.50	2.310	1.80	0.3–2.7 THz 293–333 K	HIT04 [22]

* N_2-continuum parameter was calculated using the one measured in work [7] at 137.8 GHz air-continuum parameter $5.68(5) \times 10^{-3}$ dB/km/kPa^2 enlarged by being experimentally determined at 303 K nitrogen-to-air efficiency calculated as $0.627/0.558 = 1.124$ from the data of Table 2 of Ref. [7]. Nitrogen temperature exponent is the same as for air-continuum.

The continuum absorption α_C was defined as the difference between measured total absorption α_{total} and contribution from local lines α_{local}

$$\alpha_C = \alpha_{total} - \alpha_{local} \qquad (3)$$

In our study the contribution of local lines was calculated using corresponding part of widely known Liebe's *Millimeter wave Propagation Model* (MPM) updated by Rosenkranz in 1998 [21], which contains 15 strongest water lines below 1 THz. Parameters of these lines (frequency, intensity, self- and foreign-width and temperature exponent) are given in Table 1. The line-shape function $f(\nu)$ is based on Van Vleck–Weisskopf profile and incorporates a cutoff at $\nu_c = 750$ GHz and subtracted baseline

$$f(\nu) = \begin{cases} \frac{\nu^2 \gamma}{\pi \nu_0^2} \left(\frac{1}{(\nu-\nu_0)^2+\gamma^2} + \frac{1}{(\nu+\nu_0)^2+\gamma^2} - \frac{2}{\nu_c^2+\gamma^2} \right) & \text{if} \quad |\nu-\nu_0| < \nu_C \\ 0 & \text{if} \quad |\nu-\nu_0| \geq \nu_C \end{cases},$$

$$(4)$$

where ν_0 and γ are the line center frequency and the line half width, respectively.

Since the foreign line width in [21] is related to air-broadening it has been enlarged by 11% for our H_2O–N_2 data analysis to take into account greater efficiency of H_2O–N_2 collisions than of H_2O–O_2 collisions.

An example of the calculated contribution of the local lines absorption at 143.25 GHz, temperature 55 °C and total pressure 997 hPa is shown in Fig. 2 by dashed line as a function of P_{H_2O}. It is worth noting that at experimental conditions of our study the contribution of local lines constitutes from 7% to 28% of the total absorption depending on temperature and humidity. The contribution gets larger at lower temperatures.

For the quantitative analysis of the measured continuum absorption the following empirical parameterization was utilized [6,21]:

$$\alpha_{cont}(\nu,T) = [C_{H_2O}(T)P_{H_2O}^2 + C_{N_2}(T)P_{N_2}P_{H_2O}]\nu^2 \qquad (5)$$

where $C_{H_2O}(T)$, $C_{N_2}(T)$ are, respectively, self- and nitrogen-continuum parameters at fixed temperature T. The quadratic frequency dependence of the continuum was confirmed in our experiments to the accuracy of measurements at
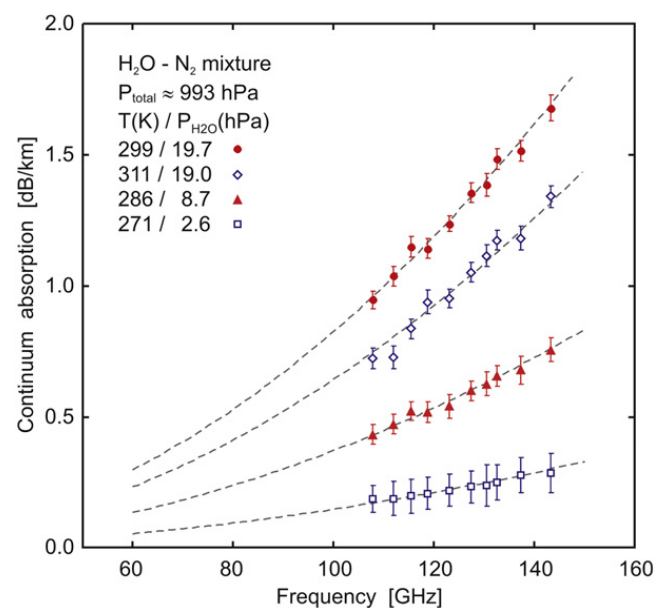

Fig. 3. Continuum absorption in a mixture of N_2 and H_2O experimentally measured at different combinations of temperatures T and water vapor partial pressures P_{H_2O} as a function of frequency. Error bars correspond to 1σ experimental uncertainties. Dashed lines are result of the ν^2-fit to experimental points.

different values of humidity and temperature (Fig. 3 demonstrates several typical dependences). It allowed averaging of the frequency-independent values $\alpha_{cont}^{exp}(\nu_i,T)/\nu_i^2$ experimentally measured at frequencies ν_i ($i=1, 2...10$) and fixed T, P_{H_2O}, P_{N_2} that leads to improvement of statistical accuracy of the continuum parameters determination by about factor of three. The averaged values of the continuum absorption normalized by ν^2 at three different temperatures are plotted in Fig. 4 as a function of water vapor partial pressure. Use of total pressure of the mixture $P_{total} = P_{H_2O} + P_{N_2}$ (that was fixed in our experiments) instead of P_{N_2} in Eq. (5) makes it a function of one variable parameter P_{H_2O}

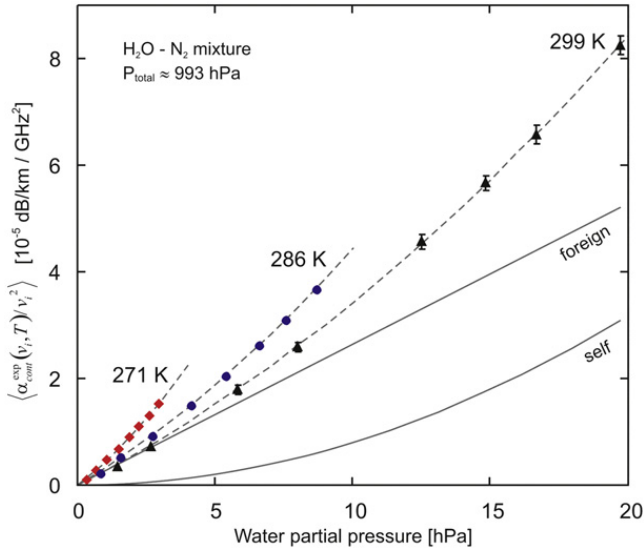$$\frac{\alpha_{cont}(\nu,T)}{\nu^2} = [C_{H_2O}(T) - C_{N_2}(T)]P_{H_2O}^2 + C_{N_2}(T)P_{total}P_{H_2O} \qquad (6)$$

Fig. 4. Averaged value of the continuum absorption normalized by ν^2 and plotted at three different temperatures as a function of P_{H_2O}. Error bars correspond to 1σ averaging uncertainty, which reflects deviation of experimental points from the ν^2-fit (see Fig. 3). For 271 and 286 K curves the error bars are of point size. Dashed lines represent the fit of Eq. (5) to experimental data. Solid lines are self- and foreign-continuum components derived from experimental data at 299 K.

Two slightly different methods were applied for further data analyses depending on the sample temperature. For the above freezing temperatures self- and nitrogen-continuum parameters were derived from the fit of Eq. (6) (adjustable parameters were C_{H_2O} and C_{N_2}) for experimental dependence of normalized continuum absorption $\langle \alpha_{cont}^{exp}(\nu_i,T)/\nu_i^2 \rangle$ on P_{H_2O}. Corresponding curves are shown in Fig. 4 by dashed lines. Self- and foreign-continuum components obtained from experimental data at 299 K are shown in Fig. 4 by solid curves. It is seen from the figure that at relatively high P_{H_2O} self- and foreign-continuum components are comparable with each other and can be accurately retrieved from the fit. At low P_{H_2O}, which is typical for below freezing temperatures the self-continuum constitutes less than 10% from the foreign-continuum and cannot be derived with satisfactory accuracy. Therefore, at below freezing temperatures the self-continuum component was not derived from the fit but calculated using results obtained at higher temperatures and subtracted from total continuum. Eq. (6) with $C_{H_2O}(T) \equiv 0$ was fitted to the residual part of the continuum absorption, which allowed determination of the foreign-continuum parameter C_{N_2} at temperatures below freezing.

Self- and nitrogen-continuum parameters experimentally measured at different temperatures are plotted in Fig. 5. Both parameters show monotone decreasing behavior with temperature increase. As it was mentioned before, at lower temperatures the self-continuum coefficient C_{H_2O} has larger uncertainty because of the minor relative contribution of this component to the total continuum absorption. The temperature dependence of the continuum parameters in millimeter wave range is usually described by the exponential law [6,21]

$$C_{H_2O}(T) = C_{H_2O}^0 \left(\frac{300}{T}\right)^{n_s+3}; \quad C_{N_2}(T) = C_{N_2}^0 \left(\frac{300}{T}\right)^{n_f+3} \quad (7)$$

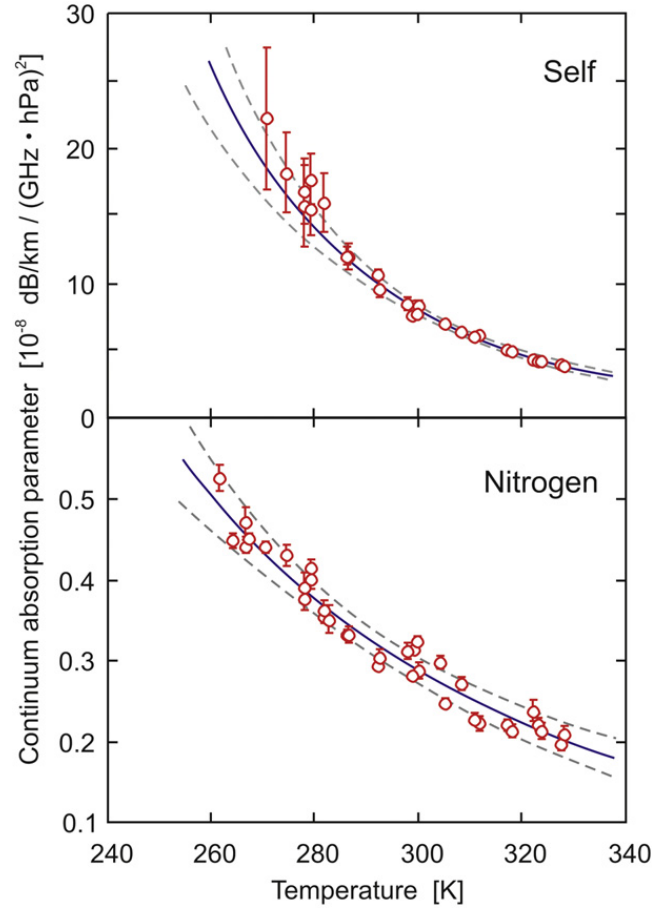**Fig. 5.** Temperature dependences of the self- and foreign-continuum parameters. Single experimental data are plotted by circles. Error bars are 1σ uncertainties. Solid lines are result of weighted fit of Eq. (7) to experimental data. Dashed lines are 99.99% confidence intervals.

where $C_{H_2O}^0$ and $C_{N_2}^0$ are self- and nitrogen-continuum parameters at 300 K, n_s and n_f are their temperature exponents. Results of the weighted least-squares fit of Eq. (7) to the experimental dependences are shown in Fig. 5 by solid lines. Weights were chosen as reversed square of the individual point uncertainty. The 99.99% confidence intervals are shown by dashed lines.

The obtained self- and nitrogen-continuum parameters as well as their temperature exponents are summarized in Table 1 along with results of some previous measurements in mm/submm range. Experimental conditions and line catalogs used for calculation of the local lines contribution are also notified.

Turning back to the question as to how the water adsorption in the resonator affects the measured continuum, we present in Fig. 6 three traces of temperature dependence of the self-continuum parameter. Two of them were measured using the classical method with only one resonator. In one experiment its length was 0.35 m, in another one 0.7 m. The third trace was obtained using the length variation method as described above. It is clearly seen that at lower temperature the water adsorption on the resonator elements introduces essential systematic error to the measured continuum absorption exceeding statistical uncertainties by the order of magnitude. Moreover the weighted least-squares fit of Eq. (7) to
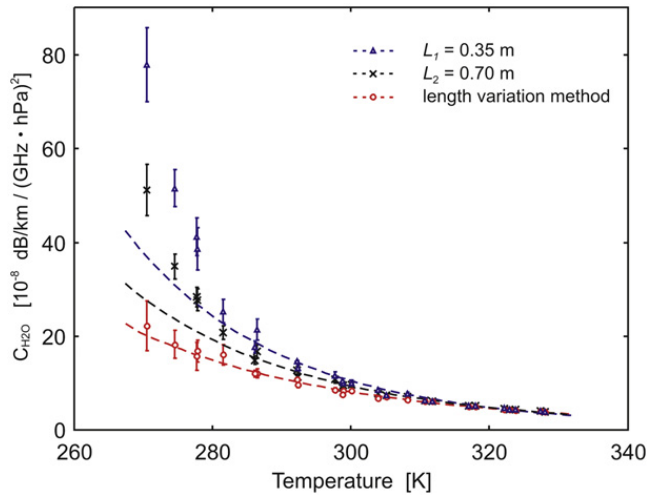
Fig. 6. Analog of Fig. 5. Temperature dependence of the self-continuum parameters obtained using one resonator at two different lengths (0.35 and 0.7 m) and by the length variation method. Dashed lines are weighted least-squares fit of Eq. (7).

the experimental data shown by dashed lines reveals strong discrepancy between the experimental points and theoretical curves at low temperatures if only one resonator is used. At the same time one can conclude that the length variation method is an efficient approach for reducing the influence of the water adsorption on result of measurements and, consequently, improvement of data accuracy and reliability. At temperatures above 310 K influence of the water adsorption is negligibly weak in comparison with experimental uncertainties and there is no need to take it into account. We would like to stress that all quantitative characteristics of the water adsorption influence are valid only for our particular configuration of the resonator; however, the qualitative picture is quite universal. It should be also mentioned that in our experiment the influence of the water adsorption on the derived foreign-continuum is negligible in comparison with its influence on the self-continuum. Use of only one resonator instead of the length variation method leads to minor changes of parameters $C_{N_2}^0$ and n_f within experimental uncertainties.

4. Discussion

Comparison of the continuum parameters obtained in this work with corresponding parameters from most known previous laboratory studies of the continuum in the same wavelength range [7,14] reveals very good general agreement. Some parameters can be considered as coinciding within the stated experimental errors (e.g., our H_2O–N_2 continuum parameters with corresponding results of [14]). Deviations of our H_2O self-continuum parameters from previous results are somewhat larger than unified uncertainties of both experiments. The $C_{H_2O}^0$ continuum coefficient is about 13% smaller than the one from work [14] but about 14% larger than the one from work [7]. The difference exceeds, declared by authors of [14,7], uncertainties by about factors of 7 and 5, respectively. In general our continuum parameters are closer to the ones from work [14]. We suppose that these

deviations originate from aforementioned water adsorption on the resonator elements, which were not taken into account in previous studies [14,7]. In view of this, smaller deviation from results of [14] can be explained by higher experimental temperatures used for the continuum study in [14] in comparison with [7]. The deviation of our continuum parameters from the results of work [7] does not really mean large difference in predicted absorption at atmospheric conditions. Even in a worse case of saturated water vapor relative deviation of the total continuum absorption calculated at atmospheric pressure in accordance with Liebe and Layton [7] does not exceed 11% within temperature range of their experiment.

It should be pointed out that similar detailed comparison of our data with results of [15] does not make sense first of all because of different range of experimental wavenumbers. To prove the statement we refer readers to Figs. 8–13 in [23], where the water dimer absorption constituting major part of the water continuum at these conditions [5] is presented. In spite of general growth the dependence of the dimer absorption in the considered range of wavenumbers (0–80 cm^{-1}) is not smooth and its satisfactory approximation by the ν^2-function is possible only in the range 0–10 cm^{-1}.

Another reason why the comparison with results of [15] would not be quite correct is different set of parameters used for the local line absorption contribution calculation. This is a second point of the discussion. As it was mentioned above, we used in this work corresponding part of MPM program [7]. This choice allows direct comparison of obtained coefficients with results of previous studies [7,14], which was important in a view of possible systematic errors related to the water adsorption. It was demonstrated in work [14] that the derived continuum parameters for the mm wave range did not vary much within reasonable choices of resonance lines dataset and lineshape function. Therefore it was decided to leave the discussion about the most accurate way of local line absorption accounting out of scope of this work. Instead of that we made empirical parameterization of experimentally measured total absorption of radiation in moist nitrogen in the studied range of temperatures and frequencies using following expression:

$$\alpha_{Total}(T,P_{N_2},P_{H_2O},f) = [(Q(T) \pm \Delta Q(T))P_{H_2O}^2 + (L(T) \pm \Delta L(T))P_{N_2}P_{H_2O}]f^{2.35}, \qquad (8)$$

where

$$Q(T) = 1.505 \times 10^{-8}\left(\frac{300}{T}\right)^{8.110},$$

$$\Delta Q(T) = \left[1.14\exp\left[-\left(\frac{T-258}{20.75}\right)^2\right]+0.03\right]10^{-8},$$

$$L(T) = 6.37 \times 10^{-10}\left(\frac{300}{T}\right)^{4.136}, \Delta L(T) = 0.18 \times 10^{-10}$$

Value of the absorption is in dB/km, frequency in GHz, pressure in hPa and temperature in Kelvin. Terms $\Delta Q(T)$ and $\Delta L(T)$ correspond to statistical experimental uncertainty.

The parameterization reproduces measured total absorption within experimental errors and allows derivation of the

continuum and its components by an interested reader using any other model of local line absorption.

The third point of the discussion is a temperature range of the continuum studies. For atmospheric applications experimental data in a very broad temperature range from well below freezing up to well above freezing are required. In spite of strong negative temperature dependence of the continuum absorption its investigation and especially investigation of the self-continuum in lower part of this range is an experimental challenge. Maximal achievable partial pressure of water vapor becomes too low due to the vapor condensation and corresponding absorption of the sample becomes too weak to measure. Additional difficulties in experiment arise from the above discussed water adsorption, which also has strong negative temperature dependence [18]. These complications are the reason why in former studies the continuum was investigated only at elevated temperatures covering less than half of the required range. Therefore, for atmospheric applications results of these studies have to be extrapolated to the low temperature part of the range. Moreover, origin of the continuum as bimolecular absorption [4] suggests uniform temperature dependence only in the range where one of the continuum constituents has dominant contribution. Thus, extension of the temperature range of experimental studies is of practical and fundamental importance. Lowest experimental temperature in works [14] and [7] was 296 K and 282 K correspondingly. In our study the water vapor self-continuum was measured down to 273 K and foreign continuum down to 261 K, which essentially broaden the range of atmospheric temperatures covered by the experimental data.

The next discussion point is comparison of obtained continuum parameters with the results of theoretical calculations of its main constituents. Dominant contribution of water dimer absorption to the H_2O self-continuum in mm range was first predicted by Viktorova and Zhevakin [24]. The prediction was supported by recent *ab-initio* calculations [23,25]. Comparison of measured self-continuum absorption with results of true bound water dimer absorption calculation [23] can be done using value of the continuum parameters determined by authors of [23]. For frequency range 0–300 GHz they obtained $C_{H_2O}^0 = 0.727 \times 10^{-7}$ (dB/km)(hPa $\times$ GHz)^2 and $n_s = 7.67$, which are about 9% lower and 50% larger than corresponding values determined in our work. In graphical form the comparison is presented in Fig. 7 at four selected temperatures within the studied range.

The comparison reveals that whole observed self-continuum at room temperature and below can be attributed to true bound water dimer absorption. At higher temperatures contribution of some other constituents of bimolecular absorption forming the continuum becomes noticeable, which agrees qualitatively with theoretical understanding of the continuum [4]. Minor excess of the dimer absorption in comparison with the measured continuum at the lowest experimental temperature may evidence slight overestimation of the dimer concentration in [23]. Some systematic excess of the measured self-continuum absorption in comparison with the
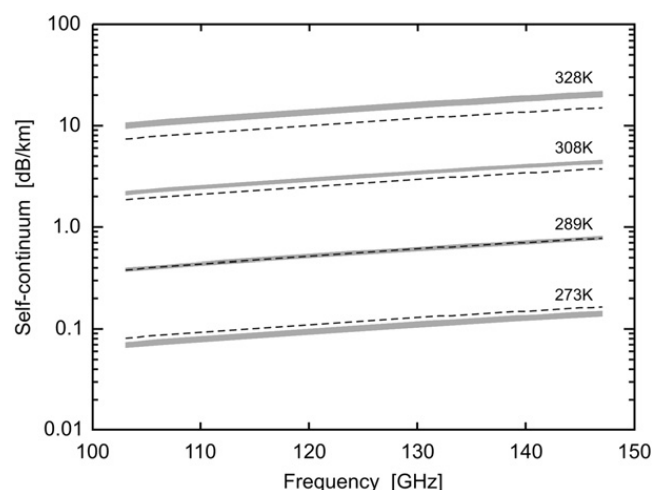

Fig. 7. Comparison of water vapor self-continuum determined in this work with water dimer absorption calculation in [23]. All data correspond to saturated water vapor absorption at each temperature. The dimer absorption is shown by dashed curves. Solid curves were calculated using the self-continuum coefficients determined in the present study (Table 1). Thickness of these curves corresponds to $\pm 3\sigma$ uncertainty range.

interpolated one, which is clearly seen in Fig. 5 at temperatures below 280 K, may be also considered as an evidence of the true bound dimer origin of the absorption. However, more sensitive investigation is required to proof this. Nevertheless, such practically perfect coincidence of measured and calculated H_2O self-continuum in [23] at studied temperatures confirms possibility of observation of the water dimer specific rotational features at equilibrium conditions at low pressure, which was proposed in work [26].

It should also be mentioned here that one of by-products of temperature range extension of the continuum studies is experimental disproof of opinion, which expects sharp growth of small water clusters number (the dimers in particular) at temperatures approaching 273 K and therefore sharp growth of corresponding absorption. Contrary to that, our data revealed monotonous, within uncertainties, behavior of the self-continuum in a whole studied temperature range confirming smooth *T*-dependence of the dimer equilibrium constant calculated in the work [27] in the range 190–390 K and used for the dimer absorption calculation in [23].

Linear in relation to water vapor pressure part of the measured continuum (H_2O–N_2 foreign-continuum) can be compared with results of calculations of the continuum arising in the H_2O–N_2 mixture as a consequence of accurate accounting of far wings of resonance water lines [28]. In fact authors of [28] calculate absorption caused by short-lived collision-induced additional dipole moment in H_2O molecule during collision with N_2. In terms of the aforementioned understanding of the continuum this corresponds to free molecular pairs contribution to bimolecular absorption. Authors of [28] also derived common coefficients of their continuum $C_{N_2}^0$ and n_f. Their values in comparison with ours are about 26% smaller and 120% larger. Frequency dependence of their continuum is not exactly quadratic, but very close. The frequency exponent
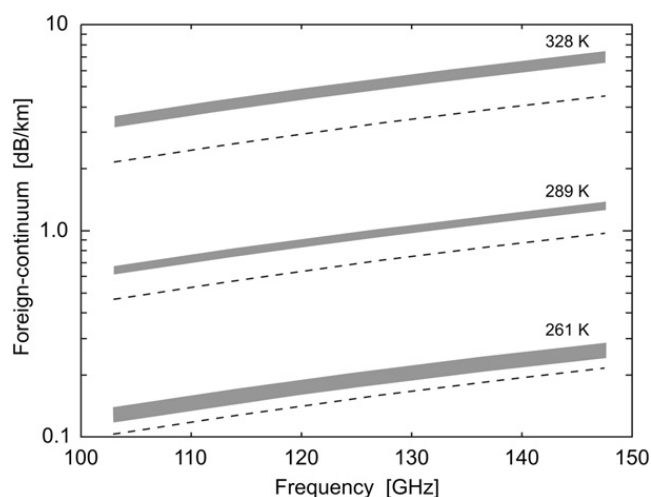
Fig. 8. Comparison of H_2O–N_2 foreign-continuum determined in this work with the continuum absorption calculated for this mixture in work [28]. All data correspond to atmospheric pressure and saturated water vapor at each temperature. The absorption calculated in accordance with [28] is shown by dashed curves. Solid curves correspond to the foreign-continuum determined in the present study (Table 1). Thickness of these curves presents $\pm 3\sigma$ uncertainty range.

is 2.059. The calculations are compared with results of our experiment at three temperatures (328, 289 and 261 K) in Fig. 8.

The figure illustrates that within the whole temperature range studied in this work the absorption calculated in [28] constitutes, as expected, only part of the observed continuum, leaving space for the other parts of the bimolecular absorption. However, stronger negative temperature dependence of continuum calculated in [28] in comparison with the observed one is difficult to explain because other continuum originating mechanisms, in particular, formation of metastable and true bound dimers are expected to supply stronger negative temperature dependence than the free-pair constituent. Moreover the free-pair constituent contribution is expected to grow with temperature and become dominant at elevated temperatures (see, e.g., [4] and references therein). These reasoning assume weaker or at least similar temperature dependence of the continuum constituent calculated in work [28] in comparison with one observed in the experiment.

5. Conclusions

Extensive experimental study of the water related continuum absorption in moist nitrogen in 107–143 GHz frequency range at accurately controlled laboratory conditions has been fulfilled. Applicability of the dual resonator method of measurement minimizing systematic errors related to water adsorption was demonstrated. The method allowed investigation of the continuum in the temperature range 261–328 K, including first-time laboratory measurements at temperatures below freezing. The study has considerably extended temperature range of laboratory-measured parameters of the continuum and improved their accuracy, which is important for fundamental understanding of the nature of the

continuum as well as for atmospheric applications including remote sensing.

One of the most important results of this study is general confirmation of the continuum parameters obtained in the work of Liebe and Layton [7] and especially in the cycle of works of Bauer with coauthors [9–14]. However, as expected, some systematic deviation of the continuum parameters and especially in the part related to the H_2O self-continuum was found. The deviation is, in our opinion, a consequence of water adsorption on the resonator elements, which was not taken into account in former experiments.

Comparison of measured components of the continuum with results of the theoretical calculations [23,28] confirms following conclusions about major physical mechanisms contributing to the observed water-related continuum at atmospheric conditions: (i) most part of the H_2O–N_2 foreign continuum can be related to short-lived collision-induced additional dipole moment in H_2O molecule during collision with N_2 (the free-pair fraction of bimolecular absorption) and (ii) practically whole H_2O self-continuum can be attributed to the true bound water dimer absorption.

Acknowledgements

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