Continuum absorption in a mixture of nitrogen and water vapor in the range from 100 to 210 GHz

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The dependence of continuum absorption on the humidity in a mixture of nitrogen and water vapor at atmospheric pressure was studied with the use of the resonator spectrometer in the frequency range from 100 to 210 GHz at temperatures of 297 and 274.5 K. It was found that the continuum absorption exhibits both linear and square dependence on the humidity at these temperatures and the values of corresponding parameters were determined. The temperature dependence of the obtained parameters was also estimated. Comparative analysis of the obtained data and the results of previous theoretical and experimental studies is presented. The possibility of eliminating systematic errors due to water vapor precipitation onto the resonator mirrors is discussed.

Introduction

The presence of water vapor in the Earth's atmosphere is one of the main causes of radiation absorption in the millimeter (mm) and submillimeter (submm) wavelengths ranges. Precise knowledge of the dependence of absorption on the atmospheric parameters make up the basis for theoretical modeling of radiation propagation in the atmosphere that are needed both for interpretation of monitoring data obtained using remote sensing from ground-based, airborne, and space-based platforms, as well as in calculating the operation ranges of radars and telecommunication systems, both ground-based and spaceborne.

More than 50 years ago it was revealed[1] by many researchers both in the field (see, e.g., Ref. 2) and laboratory (e.g., Ref. 3) experiments that absorption of mm—submm—radiation in the atmospheric transmission windows significantly exceeds that calculated as a sum of absorption profiles of all known molecular absorption lines. This excess absorption, usually called continuum, is split into two parts; one part is assigned to absorption by dry air while another one to absorption by water vapor. The second part is also split into two constituents: the first one is assigned to absorption due to interactions between water molecules (the corresponding absorption is proportional to the squared partial pressure of water vapor) and the second one being assigned to the interaction between water molecules and molecules of other gases (the corresponding absorption is proportional to the product of their partial pressures).

The majority of researchers agree that the continuum absorption is proportional to the squared frequency of radiation. In the short-wave part of the mm-range this is confirmed by the results of experiments by A. Bauer et al., generalized in Ref. 4, which are the most extensive of all the studies of continuum in the past.

In the studies by J.R. Pardo et al.[5] and V.B. Podobedov et al.[6] have shown that the dependence of continuum absorption in the submm-range is also close to the quadratic one. However, the theoretical estimates by Q. Ma and R. Tipping[7] of the continuum due to collisions of water and nitrogen molecules predicts the exponent of the power dependence on frequency to be $n_4 = 2.059$ within the 0—450 GHz range at the temperatures 220—330 K.

Despite many studies of the continuum in the mm—submm—range, the present knowledge of the problem is yet inadequate. The experimental data available are few and demonstrate large uncertainty, and often contradict each other. The temperature dependence of the continuum has been studied insufficiently. The majority of the experimental data have been obtained at warm temperatures. Extrapolation of the obtained dependences to cold temperatures, corresponding to the greater part of the Earth's atmosphere, can result in significant errors.

No universal understanding of the nature of continuum still exists. There are two leading approaches. The first one explains the continuum by imperfections in the traditional line shapes (e.g., Van Vleck—Weiskopf (VVW) shape), obtained in the approximation of collisional molecule interactions, and it is proposed within this approach a more strict derivation of the collisionally broadened absorption line profile based on quasistatic approximation, for instance.[8] The second approach considers the concentration of weakly coupled molecular complexes H_2O—O_2 and H_2O—N_2 in the atmosphere to be sufficiently high to explain the continuum within this spectral range to be due to the absorption by these complexes.[9] In this situation, an empirical

equation[4,10] is used in radiation propagation models to take into account the continuum. This equation for the nitrogen–water vapor mixture is written in the form

$$\alpha_{\text{cont}}(f, T) =$$

$$= \left\{ \left[C_{\text{H}_2\text{O}-\text{N}_2} P_{\text{N}_2} \left(\frac{T_0}{T} \right)^{n_1} + C_{\text{H}_2\text{O}-\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \left(\frac{T_0}{T} \right)^{n_2} \right] P_{\text{H}_2\text{O}} + \right. $$
$$\left. + C_{\text{N}_2-\text{N}_2} P_{\text{N}_2}^2 \left(\frac{T_0}{T} \right)^{n_3} \right\} \times$$

$$\times \left(\frac{T_0}{T} \right)^3 f^{n_4}, \qquad (1)$$

where $C_{\text{H}_2\text{O}-\text{N}_2}$, $C_{\text{H}_2\text{O}-\text{H}_2\text{O}}$, and $C_{\text{N}_2-\text{N}_2}$ are the coefficients to allow for water–nitrogen interactions, interactions among water molecules, and nitrogen–nitrogen interactions, P_{N_2} and $P_{\text{H}_2\text{O}}$ are the partial pressures of nitrogen and water vapor, T is the temperature ($T_0 = 300$ K), n_i ($i = 1, 2, 3$) are the exponents of temperature dependences for corresponding continuum components, n_4 is the exponent of the frequency dependence usually equal to 2 (Ref. 4–6, 10) or close to this value [$n_4 = 2.059$ (Ref. 7)].

Thus, obtaining new experimental data on continuum absorption are important both for refinement of empirical models and for comprehension of the continuum nature. The aim of this work is to measure parameters of the continuum, caused by the moisture in the nitrogen–water vapor mixture and, in particular, to study the frequency and temperature dependences of the continuum, using new resonator spectrometer designed at the IAP RAS.[11]

Experiment

In this study we have used the resonator spectrometer[11] and the absorption measurement technique developed in Refs. 12 and 13. To account for the instrumental function, the resonator was filled with pure nitrogen. Thus, experimentally measured absorption did not contain the nitrogen continuum [the third term in Eq. (1)]. Therefore, for parameterization of the observed continuum at a fixed temperature we made use of a simplified equation

$$\alpha_{\text{cont}}^T(f) = (C_{\text{H}_2\text{O}-\text{N}_2}^T P_{\text{N}_2} P_{\text{H}_2\text{O}} + C_{\text{H}_2\text{O}-\text{H}_2\text{O}}^T P_{\text{H}_2\text{O}}^2) f^2, \quad (2)$$

where the superscript T points out that the corresponding parameters refer to a specified temperature. The quadratic frequency dependence was used to compare our data with other data available from literature.

The absorption spectrum of the nitrogen–water vapor mixture within the frequency range of 100–210 GHz studied is formed of the absorption within the $2_{20}-3_{13}$ water line centered at 183 GHz, absorption in the far wings of other water lines, and

continuum absorption. Hence, the continuum absorption derived from the total absorption has to depend on both the model of the resonance spectral line shape used and on the number of lines involved in calculations.

Following the technique from Ref. 4, we subtracted absorption within the water lines by two methods, namely with the LIE93 model based on the list of lines and the model of atmospheric absorption by H.J. Liebe et al.,[14] known as MPM93 (VVW line profile model without cutting-off the wings), and with the model by P.W. Rosenkranz[10] (VVW profile with cutting-off line wings at 775 GHz distance from the center), hereinafter denoted as ROS98. In both of the models, the coefficients of water line broadening were 1.11-times increased as compared with the initial ones to account for more effective line broadening by nitrogen pressure in comparison with that of air.

The spectra of water vapor absorption in nitrogen at the temperature of 297 K and the pressure of 977.3 hPa obtained at six different values of relative humidity of the mixture are shown in Fig. 1 in the logarithmic scale.
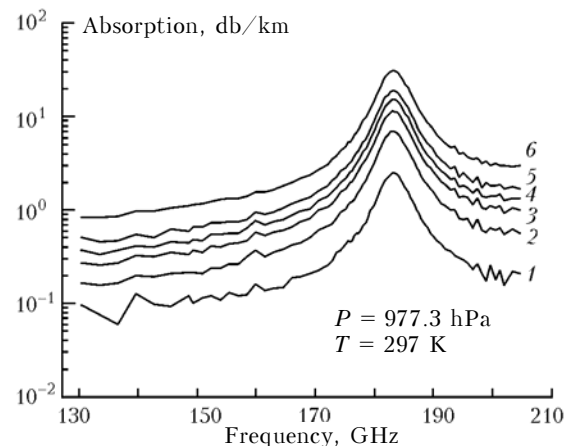

Fig. 1. Absorption spectra in the nitrogen–water vapor mixture recorded at 3 (*1*), 10 (*2*), 15 (*3*), 20 (*4*), 25 (*5*), and 40% (*6*) relative humidity of the mixture.

The parameters of water line at 183 GHz were determined from the VVW-profile approximation of each experimental record, as in Ref. 12, again, the corresponding absorption was subtracted from the experimental data.

Wings of other water line were taken into account in accordance with the lists of lines and the parameters of the above LIE93 and ROS98 models. The continuum absorption obtained at each humidity value was approximated by Eq. (2). Note, that in varying the exponent n_4 of the power-law frequency dependence, the best fitting is achieved at its values from 2.2(2) to 2.5(2) in different records, which can be either the manifestation of unknown systematic errors in the experiment (or in data processing) or of the continuum properties in this frequency range.

The dependence of the quantity in brackets in Eq. (2) on $P_{\text{H}_2\text{O}}$, obtained by the approximation, was

in its turn approximated as a sum of linear and quadratic dependences on P_{H_2O}, which allowed the coefficients $C_{H_2O-N_2}^{297}$ and $C_{H_2O-H_2O}^{297}$ to be determined. These coefficients, obtained with the use of two different models accounting for absorption in water lines, are given in the Table together with the values of the same parameters at 297 K, taken from the experimental[3,4] and theoretical[7] studies of the continuum in humid nitrogen.

Cold ambient air was used in the experiments at low temperatures for cooling the gas mixture in the resonator. The measurements were carried out in a specially equipped room on the Institute's roof. To minimize the temperature and pressure variations, the time of experiment was shortened by essentially decreasing the number of measurement points on the frequency scale. The dependence of absorption at the temperature 274.5 K and pressure 977.3 hPa on humidity of the nitrogen—water vapor mixture, which was discretely changed from 3 to 57%, was successively measured at five frequencies: 110, 125, 140, 155, 170 GHz and again at 100 GHz, for control.

After subtracting the contribution of water line wings, the obtained continuum spectrum was approximated with Eq. (2), at each humidity value, by analogy with the experiment at 297 K. The resulting P_{H_2O} absorption dependences for each frequency are shown in Fig. 2.

Insignificant random spread of the points ($\sigma \sim 0.004$ db/km), corresponding to measurements at 100 GHz for each humidity before and after measurements at other frequencies, indicates the absence of systematic humidity variations during measurements and allows estimation of statistical errors of single absorption measurements. The values of coefficients $C_{H_2O-N_2}^{274}$ and $C_{H_2O-H_2O}^{274}$, obtained like in the experiment at 297 K, are presented in the Table.

The temperature dependences of continuum absorption, i.e., the exponents n_1 and n_2 and the values of the coefficients C in Eq. (1), were determined from the solution of the set of equations

$$C_j^{300}(300/297)^{n_i} = C_j^{297}, \quad C_j^{300}(300/274)^{n_i} = C_j^{274},$$

where the index j means H_2O-N_2 for $i = 1$ or H_2O-H_2O for $i = 2$. The results are given in the Table.
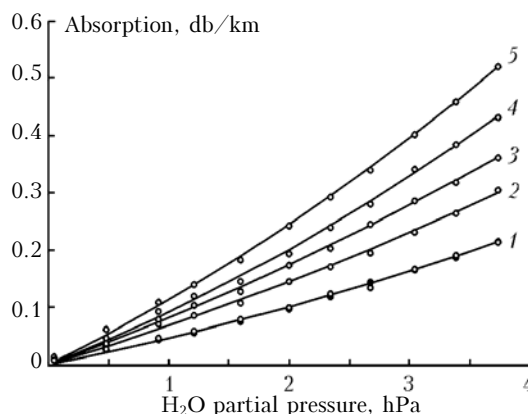

Fig. 2. Dependence of continuum absorption, obtained by subtracting the resonance absorption within water lines using ROS98 model, on the partial pressure of water vapor at 274.5 K and 996 hPa. Curves *1–5* correspond to frequencies 110, 125, 140, 155, and 170 GHz; circles — to experiment (dots on the curve *1* (110 GHz) designate the control points corresponding to the end of measurement at each humidity value); solid lines show the approximating functions.

To verify thus obtained continuum parameters, another one wide-range spectrum of the nitrogen—water vapor mixture was recorded at 259.5 K, similar to the spectra in Fig. 1. The continuum absorption, subtracted from the spectrum, agreed within the statistical error with those calculated by Eq. (1) with the use of our coefficients from the Table.

Discussion

The continuum coefficients C^{300} and their temperature dependences, obtained with the use of different models accounting for the contribution of resonance water vapor lines, agree within the statistical error (1σ). This means that the error of the account for water lines contribution, caused by either incompleteness of the list of lines or cutting-off of the line wings, is insignificant at this stage of continuum study.

Table. Continuum absorption coefficients C^{297} and C^{274}, obtained from our experiments, and the parameters C^{300} and n by model (1) compared with similar parameters from Ref. 7 (at 170 GHz), Ref. 4 (account of the line wings with the model, similar to our ROS98 model), and Ref. 3. The coefficients are given in $(db/km)/(GHz^2 hPa^2)$

Parameter	Mixture	Our experiment		Ma &Tipping[7]	Bauer et al.[4]	Liebe[3]
		LIE93	ROS98			
C^{274}	H_2O-H_2O	$3.246(310) \cdot 10^{-7}$	$3.424(322) \cdot 10^{-7}$	–	$1.874(34) \cdot 10^{-7}$	$1.345 \cdot 10^{-7}$
	H_2O-N_2	$3.633(97) \cdot 10^{-9}$	$3.999(99) \cdot 10^{-9}$	$3.357 \cdot 10^{-9}$	$4.419(124) \cdot 10^{-9}$	$3.183 \cdot 10^{-9}$
C^{297}	H_2O-H_2O	$1.334(200) \cdot 10^{-7}$	$1.375(128) \cdot 10^{-7}$	–	$0.9844(180) \cdot 10^{-7}$	$1.018 \cdot 10^{-7}$
	H_2O-N_2	$1.840(202) \cdot 10^{-9}$	$2.115(130) \cdot 10^{-9}$	$2.26 \cdot 10^{-9}$	$3.129(88) \cdot 10^{-9}$	$2.61 \cdot 10^{-9}$
C^{300}	H_2O-H_2O	$1.199(378) \cdot 10^{-7}$	$1.232(308) \cdot 10^{-7}$	–	$0.9111(166) \cdot 10^{-7}$	$0.985 \cdot 10^{-7}$
	H_2O-N_2	$1.695(274) \cdot 10^{-9}$	$1.959(205) \cdot 10^{-9}$	$2.155 \cdot 10^{-9}$	$3.002(84) \cdot 10^{-9}$	$2.548 \cdot 10^{-9}$
n	H_2O-H_2O	$8.19(309)$	$8.48(236)$	–	$5.102(190)$	0.5
	H_2O-N_2	$5.56(172)$	$5.02(109)$	1.982	$1.343(285)$	-0.5

Comparative analysis of $C_{H_2O-H_2O}$ coefficients shows that the difference between our values and those from Ref. 4 increases with the temperature decrease. The difference at 300 K is within the statistical error of 1σ. At 297 K the excess is 35% and the agreement is only within 3σ, while at 274.5 K the discrepancy is 80%, which is much larger than the measurement error. Similar comparison for $C_{H_2O-N_2}$ shows that our values are, to the contrary, essentially (50%) lower than the corresponding values from Ref. 4 at 300 K but agree within 3σ (~10%) at 274.5 K. It is worth noting good (~15%) agreement between our coefficients $C_{H_2O-N_2}$ and the results of theoretical calculations from Ref. 7. Almost all our coefficients differ from experimental data by no more than 35% except for $C_{H_2O-H_2O}^{274}$ the discrepancy for which is more than by 2.5 times. Here obtained temperature dependence for both continuum components is much stronger then in earlier studies; but due to large statistical uncertainty of our parameters it is possible to say that the difference from data from Refs. 4 and 7 exceeds the 3σ interval only a little.

Thus, the continuum absorption in the nitrogen—water vapor mixture associated with humidity was studied in the 100—210 GHz range. Quantitative wide-range measurements of the continuum of this mixture in this range at temperatures at about and below the freezing point were performed for the first time. Continuum parameters, including temperature dependence of its components, were determined. The nature of the measured absorption is in a good agreement with the data of earlier studies and the present-day conceptions of the continuum, but its temperature dependence is stronger than in other studies.[4,6–10,14] This difference can be related to the properties of continuum absorption, which appears in increasing temperature dependence at a decrease of the absolute temperature.

Another explanation of this fact can be systematic measurement errors due to condensation of water on the resonator mirrors and the corresponding decrease of their reflectivity while filling the resonator with the mixture investigated. In using traditional technique for measuring the instrumental function by means of substitution of the investigated mixture for a nonabsorbing gas, the effect of water condensation appears to be similar to additional absorption in the investigated gas mixture. The lower the temperature of the mirrors and the higher the mixture humidity, the stronger the effect. That means that the effect must manifest itself not only in a stronger temperature dependence, obtained in measurements, but in a too high value of the term $C_{H_2O-H_2O}$ describing the interaction of water molecules, which is approved by the results of our experiments.

Today, resonator spectrometers are the only instruments for laboratory studies of continuum in the long wave part of the mm—submm range. In all most known studies,[3,4,15] to determine the instrumental function, a resonator is either filled with nonabsorbing gas or degassed to deep vacuum, which results in moving off water molecules from the cavity mirrors. Use of heated mirrors[3] or high experimental temperatures[4] only decrease the effect.

The technique to account for the effect, which is based on gradual pump-out of the investigated mixture and determining the continuum as the slope of the $P_{H_2O}P_{N_2}$ product dependence on the absorption[15] does not solve the problem either.

First, it is applicable only for $C_{H_2O-N_2}$ measurements.

Second, the technique is meant for the use at very low humidity, when the quadratic humidity term can be neglected.

Third, the reflectivity of mirrors can also have a constituent, linearly dependent on $P_{H_2O}P_{N_2}$. Thus, condensation of water molecules onto the resonator mirrors is a common factor capable of influencing the continuum parameters in humid gases in the mm—sunmm range obtained in the well known laboratory experiments. To verify the hypothesis and to find the true temperature dependence of the continuum, we plan to use the cavity length variation technique[11] in further experiments, which eliminates the influence of this factor.

The main point of the technique is the following: in varying the cavity length, all instrumentation losses of radiation stay invariable while the loss due to absorption by the gas filling the cavity, grow proportional to the growth of the cavity length. Despite a significant increase of the volume and complexity of measurements, the technique allows the absorption by the gas to be measured without any preliminary recording of the instrumental function that varies at replacing the investigated gas mixture by a nonabsorbing gas.

The technique will allow significant extension of the range of working temperatures of the experiment and increase of the accuracy of determining the degree of temperature dependence of continuum. Besides, we plan to study continuum absorption in the mixture of water vapor with the second principal component of the atmosphere — oxygen.

Acknowledgements

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