On the problem of high-accuracy modeling of the dry air absorption spectrum in the millimeter wavelength range

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ABSTRACT

A detailed analysis of the dry air spectrum in the frequency range 180–260 GHz is given. The contributions of monomolecular and bimolecular absorption are discussed. It is shown that the effect of collisional coupling of zero-frequency transitions has a significant impact (up to 60%) on the value of nonresonance absorption. The coefficients of the empirical approximation of the "dry" continuum are redefined. A comparison with the continuum approximation from the Millimeter-wave Propagation Model is given.

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1. Introduction

Knowledge of the atmospheric parameters (temperature, humidity, and composition) is in demand for weather forecast and climate modeling. This information can be provided by radiometric measurements of brightness temperature. In this case, accuracy of the retrieved information is defined, in particular, by the quality of the laboratory data built into an absorption model as discussed in, e.g., [20].

Total absorption is conventionally considered semiempirically as the sum of resonance absorption and the continuum smoothly varying with frequency. High accuracy of modeling is demanded for both summands of the total absorption. However, analysis of the continuum given in [5,32] demonstrates a contradiction between the laboratory data supported by field measurements along the surface and the zenith radiometric measurement data. It is suggested that the contradiction is not related to errors in one or another measurement method, but is due to the absence of an adequate atmospheric air model. The further discussion of the question can be found in [1]. Hence, there is a global problem of developing a physically based predictive model of atmospheric absorption, which is not achievable without a clear understanding of the

basic physical absorption mechanisms and their spectral manifestation.

It is well known that water vapor and molecular oxygen are the main absorbers of radiation in the Earth's atmosphere. Both of them have resonance lines and a continuum. Several classical line profiles developed in the impact approximation are used to calculate the resonance absorption in propagation models. The Van Vleck-Weisskopf profile fits well isolated lines in the millimeter wavelength range [13]. In the case of the collisional coupling effect (also known as line mixing, interference, or spectral exchange), a Rozenkranz profile [21] or a somewhat more general function from [25] are used.

"Moist" (humidity-related) and "dry" (dry air-related) continua can be distinguished in the atmosphere. The moist continuum is essentially more intensive than the dry one, but at a height of more than 5 km the absolute humidity is virtually equal to zero, and the dry continuum contribution to the total absorption prevails in transparency windows between resonance lines.

It is known that the continuum nature is related to several intermolecular interaction mechanisms which cannot be subdivided rigorously. Their cumulative influence on the spectrum results in a significant difference between experimentally measured absorption and the resonance absorption calculated in the impact approximation.

In the millimeter wavelength range discussed in this paper, the continuum appears as "excess" absorption. It is calculated empir-

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ically when its square frequency dependence and power temperature dependence are considered. In pure gases, in usual atmospheric conditions, the continuum intensity is proportional to the pressure squared, and in a binary gas mixture it is proportional to the product of partial pressures of each component. A simplified model is used for the dry continuum calculation in propagation models (see, e.g., [15]), in which all of the continuum components related to oxygen and nitrogen intermolecular interactions are combined together, which corresponds to the continuum in a homogeneous gas of hypothetical undistinguished molecules of dry air:

$$\alpha_{cont}^{dry} = \tilde{N}(T) \cdot P_{air}^2 \cdot \nu^2 = C_{dry} \cdot \left(\frac{T}{T_0} \right)^{x_{dry}} \cdot P_{air}^2 \cdot \nu^2 \qquad (1)$$

where $C(T)$, C_{dry}, x_{dry} are empirical coefficients of the dry air continuum, ν is the frequency, P_{air} is the pressure of dry air, and T is the temperature in K; T_0 is 296 or 300 K.

It is very difficult to examine the continuum because of its weakness compared with resonance absorption, and the study of the dry continuum is even more complicated. There is a number of known measurements of the continuum in compressed nitrogen [6,7,27] and in oxygen [4]. However, to the best of our knowledge, there is only one paper [19], hereafter referred to as Paper I, dealing with experimental study of the dry air continuum at close-to-atmospheric conditions (temperature range 230–320 K and pressure range 0–3 atm) in the millimeter wavelength region (in particular, 180–260 GHz).

In what follows we present a more accurate approach to retrieve information about the dry continuum from the experimental data obtained in Paper I.

2. General approach

Modern atmospheric remote sensing applications require that spectroscopic information should be very accurate. Each factor leading to model absorption changes by more than 0.1% can be considered as significant. At such level of accuracy, air cannot be treated as an ideal gas even under usual atmospheric conditions. Relative deviation of the real pressure versus density dependence from the linear one for air can reach 0.2% for cold atmospheric layers. Therefore, the classical virial equation of the pressure versus density dependence $P = A \cdot \rho + B \cdot \rho^2 + C \cdot \rho^3 + \dots$ should be used as an equation of the gas state. Note that all coefficients are temperature dependent. Rigorous consideration requires that simultaneous interactions of all molecules with each other should to be taken into account, which is not possible at present. Fortunately, under atmospheric conditions triple collisions are rare and the binary collision approximation works well because the average distance between molecules is much longer than the characteristic molecular size [12]. Under these conditions, the total absorption can be expressed as $\alpha(\nu, \rho) = \alpha_1(\nu, \rho) \cdot \rho + \alpha_2(\nu, \rho) \cdot \rho^2$, where $\alpha_1(\nu, \rho)$ and $\alpha_2(\nu, \rho)$ are, respectively, the monomolecular and bimolecular spectra normalized to the number of the corresponding absorbers. It should be noted that such a physical meaning of terms is valid up to the uncertainty when two colliding monomers turned into a bimolecular (or pair) state. A noticeable distortion of the molecular structure occurs only at very short intermolecular distances. The colliding pair interacts with the radiation field as a single object leading to bimolecular absorption in gases. Details of this approach can be found in [24]. Such a representation of the total absorption is similar to the conventional sum of resonance and nonresonance terms, but permits a physical interpretation of the observed spectral phenomena.

2.1. Monomolecular absorption

In dry air (which is assumed to be a 79/21 mixture of nitrogen and oxygen), only oxygen has a monomolecular absorption. The pure rotational spectrum of the main isotopologue $^{16}O^{16}O$ makes an insignificant contribution to the observed absorption in the considered frequency range (180–260 GHz) but the $^{16}O^{18}O$ rotational line near 233.95 GHz is noticeable even at natural abundance of isotopes. Major sources of monomolecular absorption in this range are (i) wings of the fine structure lines (the 60-GHz band and the 119-GHz line) and (ii) the "zeroth" transitions spectrum, also called the Debye absorption. The latter appears because of the non-zero matrix element of transitions having the same initial and final states (transitions within energy uncertainty of the level) [33]. The absorption is usually modeled as a pseudo line at a zero frequency.

A significant impact of the line coupling effect on the fine structure spectrum is well known. This effect appears when closely spaced lines overlap and the collisional transitions between energy levels corresponding to these lines can occur with partial conservation of coherence. [11,21] In the case of weak coupling between lines, the effect can be taken into consideration by the first-order correction term [21], which should be added to the classical van Vleck – Weisskopf isolated line profile:

$$\alpha^{band}(\nu) = \sum_i \frac{I_{ab_i}}{\pi} \left(\frac{\nu}{\nu_{0_i}} \right)^2 \left[\left(\frac{\Delta \nu_{c_i}}{\left(\nu - \nu_{0_i} \right)^2 + \Delta \nu_{c_i}^2} \right. \right.$$
$$+ \frac{\Delta \nu_{c_i}}{\left(\nu + \nu_{0_i} \right)^2 + \Delta \nu_{c_i}^2} \Bigg)$$
$$+ \left. \left(\frac{Y_i \cdot \left(\nu - \nu_{0_i} \right)}{\left(\nu - \nu_{0_i} \right)^2 + \Delta \nu_{c_i}^2} + \frac{Y_i \cdot \left(\nu + \nu_{0_i} \right)}{\left(\nu + \nu_{0_i} \right)^2 + \Delta \nu_{c_i}^2} \right) \right] \quad (2)$$

where I_{ab} is the intensity, ν_0 is the center frequency, $\Delta \nu_c$ is the collisional width, Y is a first-order coupling coefficient, and the summation is taken over all significant spectral lines of the band.

We would like to point out that the consideration of the coupling between the zeroth lines forming the Debye absorption is of the same importance for accurate atmospheric absorption modeling as the coupling between the fine structure lines. Indeed, all the zeroth lines overlap each other completely. Moreover, zeroth transitions occur within the same energy levels between which fine structure transitions strongly coupled to each other take place. In general, spectral exchange between lines transfers intensity from the edges to the centre of the band. Thereby, the Debye absorption cannot be considered as a constant within any frequency range. After reaching its maximum in a low frequency range, the absorption should decrease when the frequency increases due to the line coupling effect.

It is worth noting that the formula proposed by Debye for the zeroth absorption is in fact the Van Vleck – Veisskopf profile with a zero center frequency. Therefore, an expression for the Debye absorption spectrum in oxygen in the zero-order coupling approximation can be obtained from the first sum of (2) at $\nu_0 = 0$:

$$\alpha_{Debye}^{band}(\nu) = \sum_i \frac{\alpha_{ab_i}}{\pi} \left(\frac{\nu}{\nu_{0_i}} \right)^2 \left(\frac{\Delta \nu_{c_i}}{\nu^2 + \Delta \nu_{c_i}^2} \right). \qquad (3)$$

It becomes apparent that taking the coupling between zeroth transitions into account requires an additional term, which is similar to the second term in (2) at $\nu_0 \rightarrow 0$ if the first-order correction is assumed:

$$\alpha_{Debye}^{band}(\nu) = \sum_i \frac{\alpha_{ab_i}}{\pi} \left(\frac{\nu}{\nu_{0_i}} \right)^2 \left(\frac{\Delta \nu_{c_i}}{\nu^2 + \Delta \nu_{c_i}^2} + \frac{Y_i \cdot \nu}{\nu^2 + \Delta \nu_{c_i}^2} \right). \qquad (4)$$
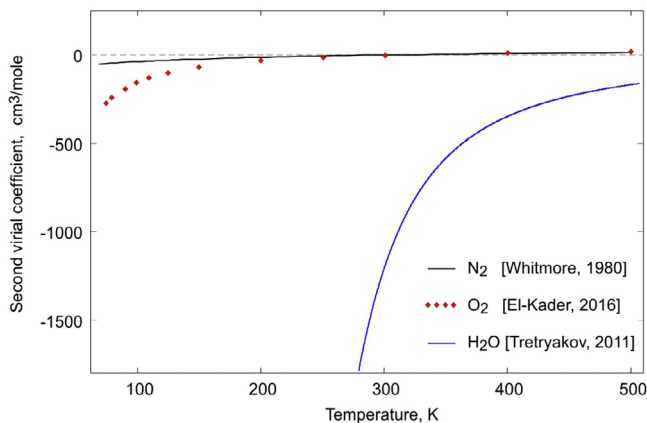
Fig. 1. Second virial coefficients of water, nitrogen and oxygen in accordance with the data reported in [30], [37] and [8], respectively.

Calculation of the monomolecular absorption for a large detuning from the resonance line center requires evaluation of the impact approximation validity. It works if the detuning is less than $1/2\pi\tau_c$, where τ_c is the collision duration, i.e., the duration of the time when the molecule "feels" proximity of the collision partner. This time can be roughly estimated as the ratio of the molecular size to the mean relative thermal molecular speed. Effective size of a molecule can be estimated, for instance, spectroscopically from a collision cross section, which can be calculated from the known pressure broadening coefficient of spectral lines. The value of 2.24 MHz/Torr [10], related to the oxygen transition with lowest rotational excitation, can be used as an upper limit. Consequently, the effective size of the O_2 molecule should be less than about 0.46 nm. It is very close to the characteristic molecule size 0.42 nm calculated as the sum of two Van-der-Waals radii 2×0.15 nm and the bond length 0.12 nm in the oxygen molecule. For a mean relative molecular speed of about 650 m/s, such evaluation results in about 230 GHz as the lower limit of the allowed (in the impact approximation) frequency detuning from the line center. This reasoning justifies our use of the models developed in the impact approximation for the monomolecular absorption calculation in this work.

2.2. Bimolecular absorption

As was mentioned, the "excess" absorption arises in a real rarified gas because of the collisional formation of bimolecular (or pair) states (free pairs, true bound and quasibound dimers). [26] In dry air, they are represented by N_2–N_2, O_2–O_2 and their hetero-pairs O_2–N_2 where the nitrogen contribution prevails in conditions under consideration. Evaluation of the relative amount of various N_2–N_2 pair states [34,35] indicates that at temperatures within 230–320 K the true bound dimers are virtually absent and the dominant states are quasibound dimers and free pairs. This is supported by the fact that in this temperature range the second virial coefficient of nitrogen has a small negative value (Fig. 1) contrary to the large negative second virial coefficient, for example, for water vapor where the presence of a significant amount of true bound dimers was experimentally confirmed [23,31]. Comparison with water vapor clearly demonstrates that the expected amount of dimers in dry air is negligible.

The difference in the quantity of true bound dimers in nitrogen and water vapor can be understood from the following simple consideration. Interaction with a third molecule is a necessary condition for the true bound dimer formation. Two monomers can form only a quasibound dimer. The translational kinetic energy of the colliding monomers partially transforms into rotation of the pair

as a whole and partially redistributes between internal degrees of freedom of the formed dimer. Pair state with almost free rotating monomers is the most probable case. The longer the time of collisional interaction, the higher the probability of the dimer formation. The nitrogen molecule has no dipole moment, and a noticeable interaction between colliding partners happens at short distances, contrary to the long-distance collisional interaction between polar water molecules. Moreover, the tetra-atomic nitrogen dimer has fewer degrees of freedom than the hexatomic water dimer and, therefore, fewer channels to redistribute and conserve collisional energy. Thus, both the probability of the formation of a quasibound dimer and its lifetime due to the spontaneous dissociation in nitrogen are less than in water vapor. Therefore, the nitrogen quasibound dimer has much less chances to interact with a third molecule. So, free pairs and highly excited quasibound dimers are prevailing bimolecular states in nitrogen under ordinary conditions.

Free pair is a bimolecular state formed in a single approach collision of two monomers. It causes a redistribution of charges in the monomers the greater, the smaller the impact parameter and the faster the approach. The corresponding transient dipole moment arises even in nonpolar molecules, so they can interact with radiation, which leads to the appearance of spectral bands exactly where they would be if the molecule had a permanent dipole. This phenomenon is generally called the collision induced absorption (CIA). Nuances and drawbacks of this term are discussed in detail in [36].

In the millimeter wavelength range we deal with a very low frequency part of the rototranslational band of CIA [9]. Even the homogeneous (determined by a short lifetime of the bimolecular state) width of the band is of the order of one terahertz. Therefore, this absorption in the considered wave range increases in proportion to the frequency squared, which is determined by the so-called radiation term.

Highly exited quasibound dimers are very similar to free pairs. The only difference is that the colliding monomers experience a few approaches to each other, but not the only one. Each monomer can be considered as an almost free rotating molecule that has an induced dipole moment interacting with the radiation. The lifetime of the monomer rotational states is very short because of the strong interaction. The dipole moment matrix element of the transitions corresponding to the rotation of the pair as a whole is small due to the monomers rotation. So, the spectrum shape of such pair states should be similar to the rotational band of free pairs, and therefore can also be approximated by the frequency dependence squared in the millimeter wavelength range.

It is noteworthy that our qualitative reasoning is consistent with the results of quantum-chemical calculations for bimolecular spectra of nitrogen reported in [3,14]. These calculations confirm that the contribution of free pairs dominates even at a temperature of 78 K.

The equation used in the modern version of Millimeter-wave Propagation Model (MPM, [22]) for dry air continuum modeling is based on the result of the nitrogen absorption calculations [3] and takes into account the factor of 1.34 corresponding to the increase in CIA in a mixture of nitrogen and oxygen [2]:

$$\alpha_{drycont}^{MPM} = 3.36 \cdot 10^{-13} \left[1 + \frac{1}{1 + \left(\frac{\nu}{450}\right)^2} \right] \left(\frac{T}{300}\right)^{-3.6} \nu^2 P_{air}^2 \,(\text{cm}^{-1}),$$

$$(5)$$

where (as well as in the following equations) the pressure is in Torr and the frequency is in GHz. Deviation of the absorption calculated by this formula from a simple square with frequency dependence under conditions of Paper I is about 3%, which is much smaller than the measurement uncertainty.
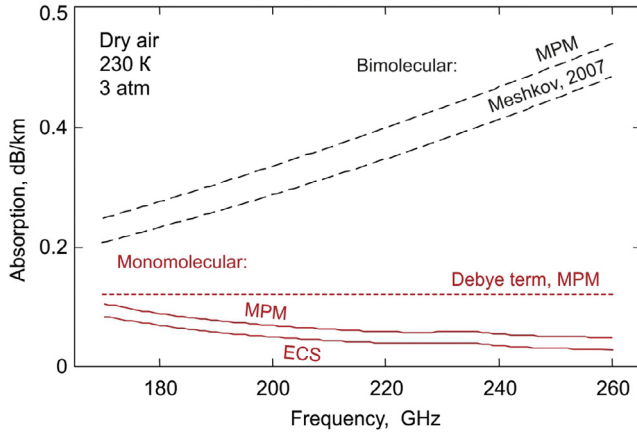
Fig. 2. Absorption components in dry air. Data from [22,18] and Paper I were used (see the text). The Debye term calculated by Eq. (6) is shown by a red dotted line for comparison with other components.

Fig. 3. Coefficient of the continuum in dry air as a function of temperature. The symbols are the values of *C(T)* calculated from pseudo-experimental data. The solid line is their approximation by a linear function. The units of *C* are $(dB/km)/(GHzTorr)^2$. The upper scale is temperature in Kelvins.

The molecules of oxygen and nitrogen are similar to each other. Both are symmetric diatomic molecules with similar masses and bond lengths. Furthermore, their quadruple moments, isotropic polarizability, and the second virial coefficients (Fig. 1) are comparable. Even though the O_2 molecule has a permanent magnetic dipole moment, the collision cross sections of O_2–O_2 and O_2–N_2 are very close to each other (compare, e.g., the broadening of the O_2 fine structure lines by pressure of oxygen and nitrogen reported in [29]. This similarity suggests that bimolecular absorption in oxygen in the millimeter wavelength range can also be approximated by a simple, quadratically frequency-dependent function. Moreover, the conclusion can be extended to the mixture of nitrogen and oxygen because O_2–N_2 pair states are formed by similar molecules.

All these arguments confirm the applicability of empirical Eq. (1) for bimolecular absorption modeling in our study.

3. Data retreatment

In Paper I, total absorption is interpreted as the sum of the Debye absorption and CIA. The Debye absorption was calculated by the following equation (formula (22) from Paper I):

$$\alpha_{deb} = 1.1 \times 10^{-8} P_{air}^2 \left(\frac{T}{300}\right)^{-2.8} \frac{dB}{km}, \tag{6}$$

where P_{air} is the dry air pressure. The equation can be obtained as a high-frequency approximation of the corresponding formula from [16]. Therefore, the authors of Paper I consider monomolecular absorption as a constant. However, calculation of this component of the absorption in dry air by MPM (Fig. 2) demonstrates an explicit frequency dependence, namely, a decrease in absorption with frequency, caused mainly by the far wings of the fine structure lines. Moreover, as was illustrated above, the Debye absorption is a constant only if the interference effect of the zeroth transitions between each other and with others lines is neglected. The effect is taken into account in the MPM by the corresponding correction of the mixing coefficients of the fine structure lines (see, e.g., Eq. (20) from [17]). Thereby, only the total absorption calculated by MPM makes sense. Due to this, the total absorption at high frequencies becomes less than the Debye component calculated by Eq. (6).

The ECS (Energy Correction Sudden) approach [28] permits a more accurate calculation of the interference effect in the fine structure lines and zeroth transitions compared with the MPM's approach. In both cases, the collisional relaxation operator matrix is used. MPM uses an analytical equation for the individual line profile, which is deduced assuming weak interference between lines (only the elements which are nearest to the matrix diagonal
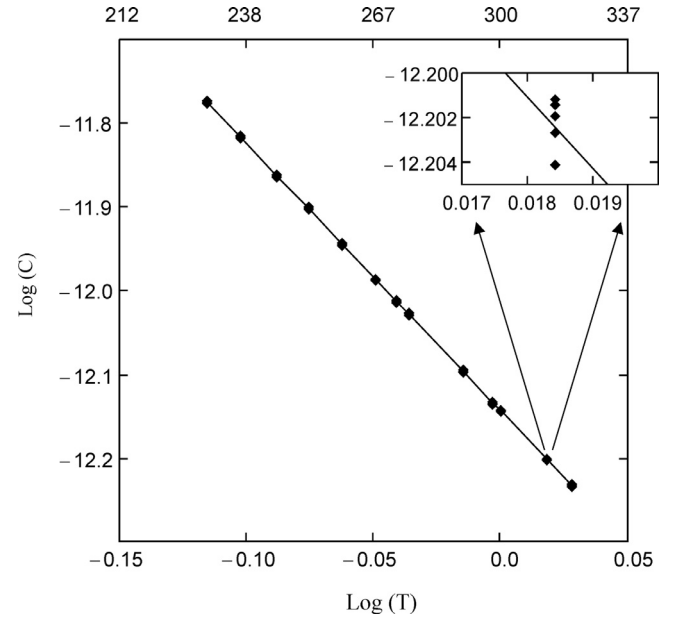
are taken into account) and absence of the interaction between different branches. ECS calculates absorption numerically with all elements of the matrix that includes all probable interactions automatically. Monomolecular absorption in dry air calculated by the ECS-13 model [18] in the 180–260 GHz range (Fig. 2) is approximately 60% less than it was considered in Paper I. Overestimation of the monomolecular oxygen absorption resulted in underestimation of the retrieved value of CIA in Paper I.

Experimentally measured total absorption was approximated in Paper I by the following formula:

$$\alpha^{dry} = \alpha_{deb} + 5.64(17) \times 10^{-13} P_{air}^2 \left(\frac{T}{300}\right)^{-3.35(11)} \nu^2 \frac{dB}{km}. \tag{7}$$

It permits the data retreatment. We calculated the total absorption used Eq. (7) for 5 different pressures and 13 temperatures, uniformly distributed within the stated parameter intervals (230–320 K and 0–3 atm). A total of 65 samples of "pseudo-experimental" data were obtained. Monomolecular absorption related to the fine structure spectrum together with the Debye absorption was modeled by ECS-13. The rotational spectrum was calculated by MPM. Such a consideration assumes the rotational lines to be isolated. This is justified due to a significant spectral separation of rotational lines from each other and from the fine structure lines (overlapping of the lines is negligible under the conditions considered). The monomolecular absorption was subtracted from the pseudo-experimental data. The remaining part of the absorption was normalized to the pressure and frequency squared. The continuum coefficients obtained by this method are presented in logarithmic scale in Fig. 3 as a function of temperature, which demonstrates their invariable power dependence on temperature.

The result of approximation of obtained data by empirical Eq. (1) is presented in Table 1 combined with the corresponding values from Paper I.

It was found that the statistical error of the continuum coefficients determination is considerably smaller than the experimental data inaccuracy given by formula (26) from Paper I. So, the uncertainty of the continuum coefficients derived in this work remains the same.

Table 1
Coefficients of eq. (1) for the dry air continuum in the 180–260 GHz range.

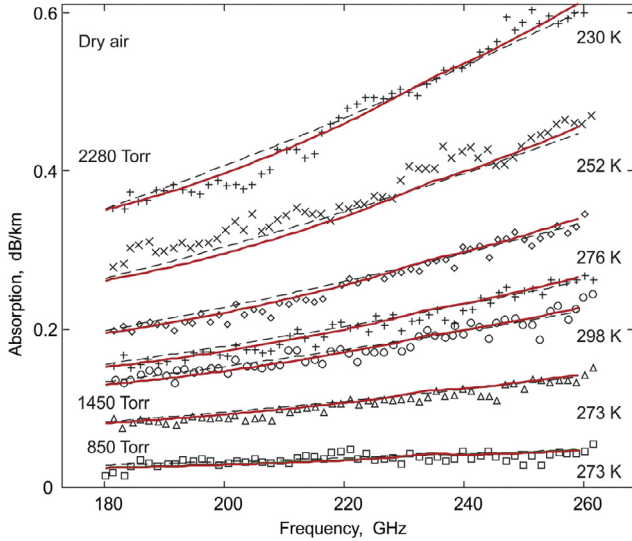| x_{dry}	C_{dry}, (dB/km)/(GHzTorr)^2	Ref.
−3.35(11)	5.64(17)·10^{-13}	Paper I
−3.22(11)	7.10(17)·10^{-13}	This work

Fig. 4. Measured absorption in dry air [19] (symbols) and its approximations by the absorption model from this work (solid red lines) and from Paper I (dashed lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 (which is an analog of Fig. 17 from Paper I) shows that, despite the essential difference of our approach, our model of the total absorption fits well the available experimental data.

4. Closing remarks

One of the results of theoretical calculations [2] is demonstration that in the millimeter and submillimeter wavelength range, CIA in dry air can be considered as CIA in N_2 at the same pressure multiplied by a factor of 0.84. This permits one to check the retrieval of bimolecular absorption in dry air using the nitrogen absorption data presented in Paper I.

The data processing method used in Paper I resulted in a 15–20% difference between the obtained coefficients of the continuum approximation $C_{air}(T)$ and $0.84 \times C_{N_2}(T)$, which is beyond the measurement error limits. Our method leads to agreement of the results within a 1σ statistical uncertainty (Fig. 5).

It is interesting to compare our data with dry continuum modeling by MPM, where Eq. (5) has been used since 2006. Direct comparison of the continuum coefficients is not possible because the coefficient corresponding to Eq. (1) in MPM is frequency dependent. For a quantitative comparison, we calculated the values of the MPM's coefficient for 180 and 260 GHz. The strip corresponding to all frequencies within this range is presented in Fig. 5 combined with the data obtained in this work. It demonstrates a reasonable agreement with our result at low temperatures, but also shows a significant (up to 20%) deviation for a hot atmosphere.

Note that the frequency dependence of function (5) is very close to quadratic. Relative difference within the frequency range 0–350 GHz does not exceed 10%. Function (5) can also be used as a dry continuum model, and its amplitude and temperature coefficients can be refined by the method described in Section 3. However, this function is based on theoretical calculations which
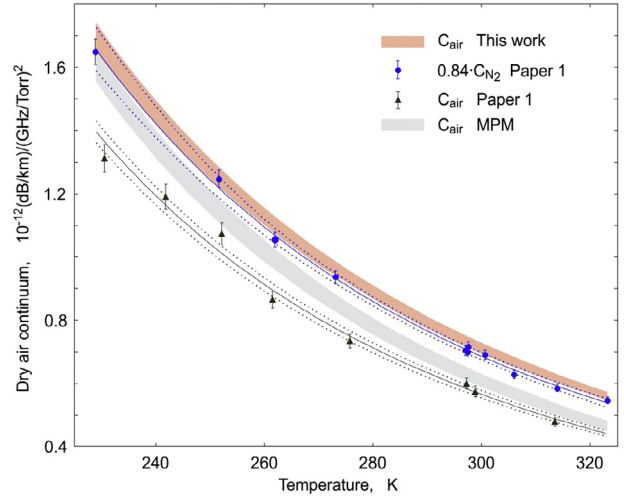
Fig. 5. Dry air continuum determined from measurements in a 79/21 mixture of N_2 and O_2 in Paper I (black triangles and solid curve), from the measurements reported in Paper 1 for N_2 using a scaling factor of 0.84 from [2] (blue bullets and solid curve) and in this work (red strip). Dotted lines and width of "this work" strip corresponds to an $\pm 1\sigma$ statistical uncertainty. The continuum calculated by MPM (gray strip, see the text for details) is given for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were not supported by accurate measurements in the millimeter and submillimeter wavelength range. We suppose that the use of function (5) is not better justified than function (1). This reasoning permits one to assume that the continuum coefficients from Table 1 can be used within a 0–350 GHz range taking into account that the uncertainty of modeling at the range edges can be increased up to about 10%. Extrapolation of the result to the higher frequencies requires additional research.

To conclude, we demonstrate that accurate calculation of oxygen monomolecular absorption (in particular, allowance for the line mixing effect between zeroth and fine structure transitions in oxygen) permits self-consistent determination of CIA in dry air and nitrogen from the experimental data reported in Paper I as provided by a theoretical result from [2]. This agreement of experimental and theoretical data suggests that the continuum coefficients obtained in this work are accurate and can be recommended for use in radiation propagation models.

References

[1] Bobryshev O, Buehler SA, John VO, Brath M, Brogniez H. Is there really a closure gap between 183.31GHz satellite passive microwave and _in-situ_ radiosonde water vapor measurements? IEEE Trans Geosci Remote 2018;56(5):1–7. doi:10.1109/TGRS.2017.2786548.

[2] Boissoles J, Boulet C, Tipping; RH, Brown A, Ma Q. Theoretical calculation of the translation-rotation collision-induced absorption in N_2–N_2, O_2–O_2, and N_2–O_2 pairs. J Quant Spectrosc Radiat Transfer 2003;82:505–16. doi:10.1016/S0022-4073(03)00174-2.

[3] Borysow A, Frommhold L. Collision-induced rototranslational absorption spectra of N_2–N_2 pairs for temperatures from 50 to 300K. Astrophys J 1986;311:1043–57.

[4] Bosomworth DR, Gush HP. Collision-induced absorption of compressed gases in the far infrared, part II. Can J Phys 1965;42:751–69.

[5] Brogniez H, English S, Mahfouf J-F, Behrendt A, Berg W, Boukabara S, Buehler SA, Chambon P, Gambacorta A, Geer A, Ingram W, Kursinski ER, Matricardi M, Odintsova TA, Payne VH, Thorne PW, Tretyakov MYu, Wang J. A review of sources of systematic errors and uncertainties in observations

and simulations at 183GHz. Atmos Meas Tech 2016;9:2207–21. doi:10.5194/amt-9-2207-2016.

[6] Dagg IR, Reesor GE, Urbaniak JL. Collision induced absorption in N_2, CO_2, and H_2 at 2.3 cm^{-1}. Can J Phys 1975;53:1764–76.

[7] Dagg IR, Anderson A, SYan WSmith. Collision-induced absorption in nitrogen at low temperatures. Can J Phys 1985;63:625–31.

[8] El-Kader MSA. Theoretical Calculation of the rototranslational collision-induced absorption (CIA) spectra in O_2–O_2 pairs. Z Phys Chem 2016;230(8):1099–109. doi:10.1515/zpch-2015-0674.

[9] Frommhold L. Collision-induced absorption in gases. New York: Cambridge University press; 1993.

[10] Golubyatnikov GYu, Koshelev MA, Krupnov AF. Reinvestigation of pressure broadening parameters at 60-GHz band and single 118.75GHz oxygen line at room temperature. J Mol Spectrosc 2003;222:191–7. doi:10.1016/j.jms.2003.08.002.

[11] Gordon RG. On the pressure broadening of molecular multiplet spectra. J Chem Phys 1967;46:448–55. doi:10.1063/1.1840686.

[12] Hartmann J-M, Boulet C, Robert D. Collisional effects on molecular spectra. Elsevier, Amsterdam; 2008.

[13] Hill RJ. Water vapor-absorption line shape comparison using the 22-GHz line: The Van Vleck-Weisskopf shape affirmed. Radio Sci 1986;21(3):447–51 May-June.

[14] Karman T, Milirdos E, Hunt K, Groenenboom GC, derAvoid Advan. Quantum mechanical calculation of the collision-induced absorption spectra of N_2-N_2 with anisotropic interactions. J Chem Phys 2015;142:084306. doi:10.1063/1.4907917.

[15] Liebe HJ, Layton DH. Millimeter-wave properties of the atmosphere: laboratory studies and propagation model. NTIA Rep 1987;87–224.

[16] Liebe HJ. MPM - an atmospheric millimeter-wave propagation model. Int J Infrared Mill Waves 1989;10:631–50.

[17] Liebe HJ, Rosenkranz PW, Hufford GA. Atmospheric 60GHz oxygen spectrum: new laboratory measurement and line parameters. J Quant Spectrosc Radiative Transfer 1992;48(5–6):629–43.

[18] Makarov DS, Tretyakov MYu, Boulet C. Line mixing in the 60-GHz atmospheric oxygen band: comparison of the MPM and ECS model. J Quant Spectrosc Radiative Transfer 2013;124:1–10. doi:10.1016/j.jqsrt.2013.02.019.

[19] Meshkov AI, De Lucia FC. Laboratory measurements of dry air atmospheric absorption with a millimeter wave cavity ringdown spectrometer. J Quant Spectrosc Radiative Transfer 2007;108:256–76. doi:10.1016/j.jqsrt.2007.04.001.

[20] Rodgers CD. Characterization and error analysis of profiles retrieved from remote sounding measurements. J Geophys Res. 1990;95/D5:5587–95.

[21] Rosenkranz PW. Shape of the 5mm oxygen band in the atmosphere. IEEE Trans Antenn Propag 1975;23:498–506.

[22] Rosenkranz PW. Line-by-line microwave radiative transfer (non-scattering). Remote Sens Code Library 2017. doi:10.21982/M81013.

[23] Serov EA, Koshelev MA, Odintsova TA, Parshin VV, Tretyakov MYu. Rotationally resolved water dimer spectra in atmospheric air and pure water vapour in the 188–258GHz range. Phys Chem Chem Phys 2014;16:26221–33. doi:10.1039/c4cp03252g.

[24] Serov EA, Odintsova TA, Tretyakov MYu, Semenov VE. On the origin of the water vapor continuum absorption within rotational and fundamental vibrational bands. J Quant Spectrosc Radiative Transfer 2017;193:1–12. doi:10.1016/j.jqsrt.2017.02.011.

[25] Smith EW. Absorption and dispersion in the O_2 microwave spectrum at atmospheric pressures. J Chem Phys 1981;74(12):6658–73.

[26] Stogryn DE, Hirschfelder JO. Contribution of bound, metastable and free molecules to the second virial coefficient and some properties of double molecules. J Chem Phys 1959;31(6):1531–54.

[27] Stone NWB, Read LAA, Anderson A, Dagg R, Smit W. Temperature dependent collision-induced absorption in nitrogen. Can J Phys 1984;62:338–47.

[28] Tran H, Boulet C, Hartmann J-M. Line mixing and collision-induced absorption by oxygen in the A band: laboratory measurements, model, and tools for atmospheric spectra computations. J Geophys Res 2006;111:D15210. doi:10.1029/2005JD006869.

[29] Tretyakov MYu, Koshelev MA, Dorovskikh VV, Makarov DS, Rosenkranz PW. 60-GHz Oxygen Band: Precise Broadening and Central Frequencies of Fine-Structure Lines, Absolute Absorption Profile at Atmospheric Pressure, and Revision of Mixing Coefficients. J Mol Spectrosc 2005;231:1–14.

[30] Tretyakov MYu, Serov EA, Odintsova TA. Equilibrium thermodynamic state of water vapor and the collisional interaction of molecules. Radiophys Quantum El 2011;5:700–16.

[31] Tretyakov MYu, Serov EA, Koshelev MA, Parshin VV, Krupnov AF. Water dimer rotationally resolved millimeter-wave spectrum observation at room temperature. Phys Rev Lett 2013;110:093001. doi:10.1103/PhysRevLett.110.093001.

[32] Tretyakov MYu. Spectroscopy underlying microwave remote sensing of atmospheric water vapor. J Mol Spectrosc 2016;328:7–26. doi: 0.1016/j.jms.2016.06.006 0022.

[33] Van Vleck JH. The absorption of microwaves by oxygen. Rhys Rev 1947;71:413–24.

[34] Vigasin AA. Bound, metastable and free states of bimolecular complexes. Infrared Phys 1991;32:461–70.

[35] Vigasin AA. Bimolecular absorption in atmospheric gases. In: Camy-Peyret C, Vigasin AA, editors. Weakly interacting molecular pairs: unconventional absorbers of radiation in the atmosphere. Netherlands: Kluwer Academic Publishers; 2003. p. 23–47.

[36] Vigasin AA. Water vapor continuum: Whether collision-induced absorption is involved? J Quant Spectrosc Radiat Transfer 2014;348:58–64. doi:10.1016/j.jqsrt.2014.06.019.

[37] Whitmore MD, Goodings DA. Calculation of second virial coefficients for nitrogen and carbon monoxide. Canadian J Phys 1980;58(6):820–7. doi:10.1139/p80-112.