



# On the origin of the water vapor continuum absorption within rotational and fundamental vibrational bands



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## ABSTRACT

Analysis of the continuum absorption in water vapor at room temperature within the purely rotational and fundamental ro-vibrational bands shows that a significant part (up to a half) of the observed absorption cannot be explained within the framework of the existing concepts of the continuum. Neither of the two most prominent mechanisms of continuum originating, namely, the far wings of monomer lines and the dimers, cannot reproduce the currently available experimental data adequately. We propose a new approach to developing a physically based model of the continuum. It is demonstrated that water dimers and wings of monomer lines may contribute equally to the continuum within the bands, and their contribution should be taken into account in the continuum model. We propose a physical mechanism giving missing justification for the super-Lorentzian behavior of the intermediate line wing. The qualitative validation of the proposed approach is given on the basis of a simple empirical model. The obtained results are directly indicative of the necessity to reconsider the existing line wing theory and can guide this consideration.

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## 1. Water vapor continuum and bimolecular absorption

It is well known that water vapor is the main absorber of radiation in the Earth atmosphere. Its spectrum includes the total contribution from the resonance lines of the atmospheric water molecules (monomers) and the non-resonant component smoothly varying with frequency. The issue of the nature of non-resonant absorption of water vapor has been debated since the moment of its discovery up to the present time, i.e., for almost a century [1–3]. Due to the absence of a physically based model, the non-resonance absorption is defined empirically as the difference between the experimentally observed total absorption and the calculated contribution of molecular resonance lines. This difference is usually called the continuum absorption or the continuum. Therefore, the continuum value depends on the way how the resonance absorption is calculated. This causes vagueness in calculation of the water vapor absorption coefficient as a sum of resonance absorption and the continuum, because the line list and the line shape parameters are updating continuously.

The most general and consistent physically based approach, which resolves the problem of the continuum in principle, was proposed by Vigasin [4]. This approach requires proper treatment of gas as non-ideal matter. In what follows we present a slightly

modified version of this approach.

It is well known (see the fluctuation-dissipation theorem [5] and the Wiener–Khinchine theorem [6,7]) that in a very general case the absorption of low-intense radiation by real homogeneous gas in equilibrium conditions is determined by the Fourier transform of the single molecule dipole autocorrelation function. The autocorrelation function characterizes the process of the dipole evolution in time averaged over all molecules. For accurate calculation of the spectrum the autocorrelation function should be: (i) determined within a very large time interval for the dipole to find itself in all states possible at given conditions, including bound states and (ii) calculated taking into account simultaneous interactions between all molecules. To obtain the absorption coefficient the spectrum should be multiplied by number density of single molecules. Obvious impossibility of such calculations requires development of various approximations separating the endless process of the dipole evolution into its elementary constituents, which entails corresponding suggestions and assumptions.

The thermodynamic equation of state of gas can be written in the virial form:

$$p = \tilde{A} \cdot \rho + \tilde{B} \cdot \rho^2 + \tilde{C} \cdot \rho^3 + \dots, \quad (1)$$

where  $p$  is the gas pressure,  $\rho$  is the gas density, and  $\tilde{A}$ ,  $\tilde{B}$ , and  $\tilde{C}$  are virial coefficients. A similar expression should be written for the total absorption coefficient of the gas:

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$$\alpha(\nu) = \alpha_1(\nu) \cdot \rho + \alpha_2(\nu) \cdot \rho^2 + \alpha_3(\nu) \cdot \rho^3 + \dots, \quad (2)$$

where  $\nu$  is the frequency and  $\alpha_1, \alpha_2, \alpha_3 \dots$  are the normalized spectra (note that they also are density dependent functions due to, for example, collisional broadening of spectral lines) characterizing single molecules, their pairs, trios, etc.

In a simplest approximation of ideal gas, there is only the term changing linearly with density in both equations. The molecules are not interacting with each other but their instant collisions randomly change the phase of their dipole oscillations. Therefore, it is sufficient tracing the single dipole motion only until the first collision. The gas contains only monomers having internal energy distributed according to the Boltzmann law. The resulting spectrum is the sum of Lorentzians. All effects related to the features of pair intermolecular interaction potential, such as the line center pressure shifting, spectral exchange, speed dependence of relaxation, etc. and non-resonance absorption including all its possible constituents are absent. For their physical justification (as well as for justification of the rotational dependence of pressure broadening) the next approximation of the gas non-ideality should be taken into account. The estimations show (see, e.g., [8]) that in usual conditions addition of the term of the series expansion changing quadratically with density is sufficient at the modern level of measurement accuracy. This implies that consideration of pair interactions between molecules and all the corresponding processes in gases is sufficient for interpreting the results of spectroscopic study. For a comprehensive allowance for pair interactions one should take into account (i) the specifics of collisions of monomers with each other and (ii) pair molecular states [9] including collisionally formed doubled molecules (dimers) in true bound and quasibound states and free molecular pairs. By the “monomer” we understand a single molecule moving in the field of a pair interaction potential between two sequential collisions. By the “free-pair” we understand a couple of single molecules, which approach each other only once during the collision. Important: free-pairs must noticeably contribute to the second virial coefficient contrary to the weak collision between two monomers which is similar to colliding molecules in ideal gas. The “true bound dimer” is a molecular pair whose total internal energy is below the lowest dissociation limit. The dimers having internal energy above the dissociation are referred to as “quasibound” (or “metastable”).

Note that dimers and free-pairs do not interact with anything else in the binary approximation (triple and higher order interactions are ignored). The average time between the dephasing collisions of a dimer with a neighboring molecule can be introduced by analogy with two monomers collision in the ideal gas approximation.

In accordance with the accepted definition of the monomer its line is the spectrum of the process characterized by the corresponding dipole autocorrelation function. We have to restrict this process in time because the molecule can couple with its collisional partner and temporally stop being a monomer. It seems reasonable to stop tracing the process at the moment when the phase shift of the dipole oscillations induced by intermolecular interaction reaches  $\pi$  or more, which means quite complete decorrelation with the initial process. The obtained line shape should be multiplied by the relative number of monomers at the given state. The sum of all monomer lines is its normalized spectrum. The spectrum multiplied by the monomer number density gives the first summand of Eq. (2). Note that the number of monomer collisions per unit time grows linearly with gas density. That is why pressure shifting, speed dependence and other manifestations of pair collisions in resonance line shape depend linearly on pressure until the second term in Eq. (1) becomes significant. Our monomers are not free molecules. They are permanently moving

in the field of the interaction potential and, rigorously speaking, should be considered within pair states. However, linearity of the aforementioned collisional manifestations confirmed experimentally in a very broad range of pressures (from a small fraction of Torr up to atmospheric pressure) evidences that the monomer dipole evolution process occurs without noticeable change of molecular structure so the monomers are almost free.

The second term in Eq. (2) corresponds to the absorption related to processes occurring with pair molecular states. Their concentration is proportional to the squared density of monomers. We point out that with our definitions it is not the density-quadratic correction to the monomer spectrum. Pair states can be regarded to be different from monomers absorbing objects. The most obvious case confirming this statement corresponds to true bound dimers. Their spectrum is the first part of the second summand of Eq. (2). Bound dimers, in spite of their extreme flexibility, do not differ, in principle, from any usual molecule. Their spectrum is characterized by the process of evolution of a joint dipole of the double molecule in the time interval between two successive collisions. The spectrum shape can be calculated, for example, employing: (i) quantum chemistry methods for determination of a complete set of stationary states and dipole matrix elements of corresponding transitions and (ii) empirically determined collision cross-section between dimers and other molecules. Multiplication of the spectrum by the dimer number density will give the dimer absorption coefficient, which should be added to the monomer absorption coefficient as if you want to calculate the spectrum of a gas mixture. The spectrum of quasi-bound dimers (which is the next part of the second summand of Eq. (2)) can be calculated, in principle, analogously but requires evaluation of the dimer lifetime in all possible states. The third (last) part of the second summand of Eq. (2) is the contribution of free-pairs. It is the spectrum of the process characterized by the time evolution of the dipole formed by all charges of two colliding molecules. This process is also limited in time. It begins when molecules approach each other and finishes when they fly away. For certainty one may choose the starting moment when distortion of initial oscillations of the dipole of each molecule is, for example,  $\pi$  or less. The Fourier-transform of the autocorrelation function of the joint dipole will give a spectrum shape, which should be multiplied by a relative fraction of free-pairs under given thermodynamic conditions.

Note that the total number of pair states in general and the number of free-pairs in particular are limited from above by the value of the second virial coefficient. The relative number of these states is as small as the ratio of the second to the first term of Eq. (1). The pair states distribution can be calculated, for example, following the ideas from the work [10]. The total relative number of the pair (triple, etc.) states can be evaluated on the basis of the value of the second (third, etc.) virial coefficient of Eq. (1). For water vapor, these coefficients can be calculated in the temperature range from 0 °C to 1250 °C based on high-accuracy (estimated uncertainty is less than 0.1%) empirical data on the dependence of density on pressure [11,12]. The results of such calculations can be found, e.g., in the work [8]. They demonstrate in particular that under room conditions (296 K, 60% RH), the relative numbers of the double and triple states are evaluated as  $8.9 \times 10^{-4}$  and  $2.3 \times 10^{-6}$ , respectively, so only the monomolecular and bimolecular terms in (2) are really significant. We realize that subdivision into monomolecular and bimolecular absorption may be difficult in boundary cases mostly related to free-pairs. The reasoning below allows suggesting that the contribution of such cases is of the next order of smallness. The collision cross-section radius of H<sub>2</sub>O molecule averaged over rotational states is about 10 Å in water vapor under usual conditions. This gives an estimate of the distance between collisional partners when the

absorber dipole motion becomes uncorrelated with its initial oscillations. At this stage the process determining the shape of the monomer line (including near, intermediate and far wings) is practically over. The time passing after this moment until reaching the nearest distance between the colliding molecules (moving with mean relative thermal speed) is much longer than the characteristic free-pair state lifetime, which follows from typical shape of experimentally observed spectra of collision induced absorption in non-polar gases. Therefore, the process resulting in noticeably different from zero values of autocorrelation function of the joint dipole of two molecules occurs at much shorter times and distances ( $\sim 1$  Å or less) between colliding partners. Only such a close interaction leads to sufficiently significant redistribution of their charges, leading to induced dipole and observed collision induced absorption [13]. This implies that with given definitions free-pairs can not notably contribute to the intermediate and far wings of monomer lines.

To conclude this part we suggest explicit calculation of the density-linear component of series expansion (2), which we call monomolecular absorption, instead of using the impact approximation for the monomer line shape and looking for density-quadratic corrections to the far wings related to bimolecular absorption. This is the major difference from the former approach. In the remaining part of this section we demonstrate the problem faced using the previous approach of the continuum interpretation.

The first term of (2) is a sum of the monomer line profiles. Within the impact approximation used in the former approach, the profile is very close to Lorentzian (or, more generally, the Voigt profile). The impact approximation limits the profile validity for frequency detuning off the line center much less than  $1/2\pi\tau_c$ , where  $\tau_c$  is the duration of a collision. The duration of a collision is about  $10^{-12}$  s (see, e.g., [14,15]). So the shape of the wing should become non-Lorentzian at detuning of  $2\text{--}5\text{ cm}^{-1}$ . However, the wings of the Lorentzian (or equivalent) profile are usually cut off at  $25\text{ cm}^{-1}$  following [16].

The second term of Eq. (2) corresponds to bimolecular absorption including spectra of dimers in true bound and quasibound states and free-pairs [4,9,17]. Considerable contribution of dimers to the water vapor continuum was suggested by two research groups for the millimeter-wave [18] and IR [19] ranges in the middle of the 1960s. Only recently, this hypothesis has been confirmed by detecting “fingerprints” of the dimer in the spectrum of equilibrium water vapor in the millimeter-wave range [2,20,21]. The results of analyzing the temperature dependence of the continuum spectra in the ro-vibrational bands of water monomer [17] also give an evidence of the dimer nature of the continuum. In the both cases, the number of dimers was found to be in good quantitative agreement with the second virial coefficient. These results experimentally confirmed that the term proportional to  $\rho^2$  in (2) should not be neglected. In both cases the authors demonstrated that the true bound dimers can be responsible for only part of the observed continuum, while the rest should be explained by other mechanisms. The most probable contribution seems to be that of the metastable dimers without which no bound dimers can be formed and whose relative number (under the usual conditions of the Earth atmosphere) should be nearly equal to that of the bound dimers [4,10].

The number density of the bound and metastable dimers can be calculated using the values of the dimerization constants:

$$n_D = K_D p_m^2 / kT, \quad (3)$$

where  $n_D$  is the dimer density,  $K_D$  is the dimerization constant,  $p_m$  is the partial pressure of the water monomers,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. In the formula (3),

$$n_D = n_{Db} + n_{Dm}, \quad K_D = K_{Db} + K_{Dm}, \quad (4)$$

where  $n_{Db}$ ,  $n_{Dm}$ ,  $K_{Db}$ , and  $K_{Dm}$  are the number densities and dimerization constants of the bound and metastable dimers, respectively.

The total number of the pair states is determined by the second virial coefficient  $B$ , which can be expressed as the sum of the coefficients corresponding to different types of the molecule pair states [9]:

$$B(T) = B_b(T) + B_m(T) + B_f(T) = -K_D(T)RT + b_0(T), \quad (5)$$

where  $b_0$  is the excluded volume, which corresponds to interaction of molecules without the dimer formation, i.e., free-pairs, and  $R$  is the universal gas constant. The value of  $B(T)$  for water vapor can be determined using numerical parameterization from [8]. For the estimation of  $b_0(T)$  we used the data from [22], which were obtained on the basis of the classical concepts with using the most accurate to date full-dimensional potential energy surface of the water dimer determined from *ab initio* calculations. These data are in excellent agreement with all known empirical thermodynamic data (see, e.g., [8] and Refs. therein). To the best of our knowledge, no any other estimation of  $b_0$  is available, but results of the paper [23] confirm that properly calculated  $b_0(T)$  retain its intuitive physical meaning and is in a good agreement with thermodynamic data. We would like to emphasize that a very small value of  $b_0$  in usual conditions in comparison with the other term in (5) makes the impact of its possible uncertainty absolutely negligible in our further evaluations.

The value of  $K_{Db}$  as a function of the temperature was reported in several studies (see, e.g., [24–26], and Refs. therein). We used slightly corrected (as will be explained below) results of *ab initio* calculations [25] mainly because they had been confirmed by experimental observation of the dimer spectrum [21] with statistical uncertainty of about 10–15%. However (taking into account the complexity of the spectrum analysis and indirectness of the method of measurements), we admit that the obtained value can be somewhat systematically overestimated because of quite uncertain contribution of quasibound states of the dimer. Possible overestimation of  $K_{Db}$  is indirectly indicated, for example, by calculations reported in [24,26]. We took into account that the dimer dissociation energy  $D_0 = 1234\text{ cm}^{-1}$  was used in the calculations [25]. At the present, the most accurate value of  $D_0$  determined on the basis of the experimental data [27], is equal to  $1105(10)\text{ cm}^{-1}$ , which is in a good agreement with a value of  $1108\text{ cm}^{-1}$  obtained by the recent *ab initio* calculations [28]. Since  $K_{Db} \sim \exp(D_0/kT)$ , the correction factor for parameterization of the dependence  $K_{Db}(T)$  [25] has the form  $\exp(\Delta D_0/kT)$ , where  $\Delta D_0 = (1105 - 1234)\text{ cm}^{-1}$ . Allowing for this correction, we obtain

$$K_{Db}(T) = 4.7856 \cdot 10^{-4} \cdot \exp(1669.8/T - 5.10485 \cdot 10^{-3}T) (\text{atm}^{-1}). \quad (6)$$

Using formulas (4)–(6), the values of  $B$  from [8] and  $b_0$  from [22] for a temperature of 295 K, which will be used in what follows herein, we obtain:  $K_{Db} = 0.0305\text{ atm}^{-1}$  and  $K_{Dm} = 0.0254\text{ atm}^{-1}$ .

Based on these values and formulas (3) and (4), one can obtain a formula for the spectrum of the dimer absorption coefficient including the true bound and metastable states:

$$\alpha_{\text{dimer}}(\nu) = (K_{Db} \alpha_{\text{bound}}(\nu) + K_{Dm} \alpha_{\text{metastable}}(\nu)) \cdot p_m^2 / kT, \quad (7)$$

where  $\alpha_{\text{bound}}(\nu)$  and  $\alpha_{\text{metastable}}(\nu)$  are the spectra of the absorption coefficients of the bound and metastable dimers, which are normalized to the density, respectively.

The most accurate current quantum chemical calculations of the bound water dimer spectrum up to a frequency of  $600\text{ cm}^{-1}$  were made by Scribano and Leforestier [29]. They were confirmed by later calculations performed up to  $1000\text{ cm}^{-1}$  by another group

using a different method [30]. Except for some insignificant issues, calculation [29] agrees well with the experimental data in the millimeter-wave [20,21] and far infrared [31] ranges and, therefore, they are quite appropriate for the continuum analysis.

For higher frequencies, i.e., in the region of the fundamental ro-vibrational bands of the water molecule (centered near 1600, 3660, and 3760  $\text{cm}^{-1}$ ), a simplified model of the bound dimer spectrum was proposed [17]. In this model, the bands of the ro-vibrational spectrum of dimers are described by the Lorentz profile with an experimentally fitted full width at a half maximum (FWHM) of 60  $\text{cm}^{-1}$ , and their central frequencies and integrated intensities are taken from the calculations based on the perturbation theory [32] and the experiments in neon matrices [33] and helium nanodroplets [34]. Although this model can only approximately correspond to the profile of the bands, and their integrated intensities are known with an uncertainty of  $\sim 20\%$ , estimation of the water molecule dimerization constant, which was obtained analyzing the experimental spectra, was found in [17] in good agreement with the most accurate available data.

The quantum-chemical calculation of the spectrum of metastable dimers is impossible so far. However, its shape and intensity can be evaluated based on the fact that this state is intermediate between two free molecules and a stable dimer. In one limiting case, the dimer in the metastable state interacts with an electromagnetic wave as two unbound monomers freely rotating near each other, and in the other case, its spectrum is identical to that of the bound dimer [35]. In both cases, the short lifetime of the metastable state determines strong homogeneous broadening of the spectrum (according to the estimations given in [17] the half-width of the resonance lines should be within 7–20  $\text{cm}^{-1}$ ). Practically the same approach to the bound and quasibound dimer absorption modeling in pressurized water vapor spectra in the 3000–4500  $\text{cm}^{-1}$  range was successfully employed in the work [36] that can be considered to some extent as quantitative validation of the approach.

Analysis of the experimental data on the water vapor continuum in the spectrum regions under consideration, which will be presented in detail below, shows that the experimentally measured absorption significantly exceeds the absorption calculated by Eq. (7) for any method of evaluating the metastable-dimer spectrum. In the millimeter-wave band this difference can reach 50% depending on the model [21]. The same trend was observed as a result of analysis of the water vapor absorption in the range from 15 to 200  $\text{cm}^{-1}$  [31]. The same problem was also revealed in the IR range after our reanalysis of the continuum data from [17]. Initially the experimentally found continuum was interpreted as a cumulative contributions of the bound and metastable dimers [17]. Obtained ratio between the numbers of metastable and bound dimers near room temperature amounts to about 2, while the values of the dimerization constant  $K_{Db}$  and the second virial coefficient indicate that this ratio should be near 0.8 pointing out that the number of quasibound dimers was overestimated significantly. The problem was confirmed in [37] stating “that continuum absorption cannot be fully accounted for by the bound and quasibound components”. The remaining part of the continuum, which cannot be related to either the bound or metastable dimers, amounts to 20–50%, depending on the spectral band. Note that taking into account the aforementioned possible overestimation of the dimerization constant only increases the gap between the observed and the simulated continua and enhances the problem of the “excess” continuum.

Along with the dimers, the free molecular pairs can contribute to bimolecular absorption (the  $b_0$  component in the second virial coefficient). According to the available estimations [10], the number of the free-pair states near room temperature is negligibly small compared with the number of the dimer states. The free

pairs are responsible for the absorption which is due to formation of an additional short-term transient dipole moment induced during the collisional interaction of molecules. In gases of non-polar molecules this type of absorption is called “collision-induced absorption” (see [38] and Refs. therein), but very often the term is also used for corresponding absorption in gases of polar molecules. The contribution of this absorption to the water vapor continuum in the range of the  $\text{H}_2\text{O}$  rotational band was evaluated in the work [39]. The authors neglected the pair states distribution and treated all molecular pairs as free-pairs. Nevertheless, the obtained absorption was found to be negligibly small in comparison not only with the total monomer absorption but with the observed continuum too. A similar conclusion was made in the work [13] based on the analysis of *ab initio* data on collisionally induced dipole moment in  $\text{H}_2\text{O}$  [40]. The contribution of free-pairs to the observed continuum is so small that even when increased by two orders of magnitude (which would contradict all known data) it will not resolve the problem.

Thus, the bimolecular term in (2) does not allow explaining the observed continuum without looking for another absorption mechanism. The only remaining one, which may be responsible for the “excess” part of the continuum, is, in our opinion, underestimated monomolecular absorption in the region of the intermediate wings of the resonance lines, which cannot be predicted by the currently available models with sufficient accuracy. The mechanism responsible for the “excess” continuum should be the same in all considered bands due to predominant relaxation of rotational states during collisions [41]. Satisfactory description of the continuum by some universal model for all spectral ranges would evidences in a favor of correctness of our hypothesis. The next section of the paper presents an example of constructing such a model. Note that the development of a precise, physically based model of the line profile does not make sense at this stage and is very far beyond the scope of this work. Our current intention is only to draw the attention of the interested researchers to the existing problem and outline methods for its possible solution. We suggest to calculate the process of the monomer dipole evolution when the molecule is approaching its collisional partner using modern numerical methods. The classical trajectory calculation method (see [15] and references therein) employing high accuracy interaction potential can be used. Averaging of the calculated trajectories over the impact parameter, relative speed, states of the perturber, etc. allows obtaining the monomer dipole autocorrelation function. The function will determine the shape of the monomer resonance line taking into account details of the collision process. The number of turns made by the monomer during the collision obviously depends on its rotational state. Therefore the line wing shape (by the analogy with its collisional width) should be a function of the molecule rotational state. We will be able to develop the physically based semi-empirical model of line shape including near, intermediate and far wings after we obtain results of such numerical calculations in a broad range of rotational quantum numbers.

## 2. Empirical model of the intermediate and far line wings

The idea about the necessity of adjusting the shape of the intermediate and far wings of monomer lines to describe the entire observed continuum was brought forward rather long ago [16]. The theoretical calculations of the far wings of the resonance lines beyond the impact approximation are presented in the works by Tvorogov and co-workers [42,43]. This approach allows one, in principle, to describe quantitatively the continuum absorption, which is considered as a monomolecular one. This implies a linear relationship between pressure and density, which is typical for the



ideal gas approximation. The approach is not widely used because of the presence of a great number of empirical parameters.

A well known semi-empirical model of the atmospheric continuum was developed by Clough, Kneizys and Davies (CKD model) [44]. It was later modified to the MT\_CKD model (Mlawer–Tobin–Clough–Kneizys–Davies) [45]. The authors of the CKD model also believe that the continuum is of exclusively monomolecular origin. The CKD model is based entirely on the assumption that the continuum is formed by uncertain absorption in the intermediate and far line wings. In particular, that was the reason for including the “pedestal” of the resonance line in the continuum, which ensures continuity of their model, (see, e.g., Fig. 1 in [44]). The MT\_CKD modification of the model includes additional term which is supposed by the authors to be responsible for the collision induced absorption. The term is calculated as slightly modified line by line sum of a short time broadened monomer lines. The both terms are multiplied by the monomer concentration for calculation of the absorption and, therefore, represent in fact just semi-empirical modeling of the monomolecular absorption.

The CKD model is based on the use of the empirical correction  $\chi$ -function which modifies the intermediate and far wings of the resonance lines. The formula for the coefficient of the continuum absorption normalized to the number density of the water molecules is written as

$$C(\nu) = \sum_i R(\nu, \nu_i) S_i (f_c(\nu - \nu_i) \chi(\nu - \nu_i) + f_c(\nu + \nu_i) \chi(\nu + \nu_i)), \quad (8)$$

where  $R(\nu, \nu_i)$  is the normalized radiation term

$$R(\nu, \nu_i) = \frac{\nu}{\nu_i} \frac{\tanh(h\nu/kT)}{\tanh(h\nu_i/kT)},$$

$h$  is the Planck constant,  $S_i$  are the integrated intensities of  $\text{H}_2\text{O}$  lines,  $\nu_i$  are the central frequencies of these lines, and  $f_c(\nu \pm \nu_i)$  are the “cut-off” line wings:

$$f_c(\nu \mp \nu_i) = \begin{cases} \frac{1}{\pi} \frac{\Delta\nu_i}{\nu_{\text{cut}}^2 + \Delta\nu_i^2}, & |\nu \mp \nu_i| \leq \nu_{\text{cut}} \\ \frac{1}{\pi} \frac{\Delta\nu_i}{(\nu \mp \nu_i)^2 + \Delta\nu_i^2}, & |\nu \mp \nu_i| > \nu_{\text{cut}} \end{cases}. \quad (9)$$

In Eq. (9),  $\Delta\nu_i$  is the collisional half-width of the lines, and  $\nu_{\text{cut}} = 25 \text{ cm}^{-1}$  is the wing “cutoff” frequency. If the Doppler line width is comparable with the collisional one, then the Voigt profile should be used instead of the Lorentz one. In the IR range, one can approximately set the radiation term equal to unity, and in the millimeter-wave range, it is approximately equal to  $(\nu/\nu_i)^2$ .

Thus, if the function  $\chi(\nu - \nu_i)$  is equal to unity, then the continuum includes only the summarized cut-off parts of the Lorentzian profiles of the  $\text{H}_2\text{O}$  lines.

When the  $\chi$ -function was constructed, the finite time of the molecular collision duration was taken into account. Due to this, the line wing should be sub-Lorentzian at a large detuning off the center ( $> 100 \text{ cm}^{-1}$ ). This ensures agreement with the experimental data on the absorption in the transparency windows between the bands of the water vapor spectrum, which is much weaker than the total Lorentzian contribution from the resonance lines. In the transparency microwindows between the resonance lines within the bands the continuum may exceed the total contribution from the line wings several times, even if these wings are Lorentzian. Describing this absorption by adjusting the line shape requires that in the range of the detuning from the center exceeding  $5\text{--}15 \text{ cm}^{-1}$ , the wing should pass above the Lorentzian (super-Lorentzian wing).

Allowing for the aforesaid, the  $\chi$ -function used in the CKD model [44] has the following form: for zero detuning, it is equal to

unity then it increases to about 10 for a detuning of  $25 \text{ cm}^{-1}$ , and falls to zero for greater detunings.

Herein, when choosing an empirical model to describe the line wings, we base our consideration on the following ideas: (a) part of the continuum is determined by the water dimers, (b) the shape of the intermediate and far line wings is not known, but it is confirmed experimentally that near the line center (at detuning from about 2 up to about 20 widths) the wing is Lorentzian with a high accuracy (a difference of  $\sim 0.1\%$ ), (c) it follows from the calculations and from the experimental observations that the wing should be sub-Lorentzian at very large detuning values ( $\Delta\nu > 1/\tau_c$ ), (d) if the collision duration is evaluated as the time, during which a molecule is moving with an average thermal relative speed and covering a certain distance, then a detuning of  $25 \text{ cm}^{-1}$  at room temperature corresponds to the distance of  $1.8 \text{ \AA}$ , which slightly exceeds the characteristic geometric size of the  $\text{H}_2\text{O}$  molecule ( $\sim 1.4 \text{ \AA}$ ), but is shorter than the radius of the excluded volume ( $\sim 2.5 \text{ \AA}$ ) and significantly shorter than the radius of the efficient collision cross-section determined by the spectroscopic methods ( $\sim 10 \text{ \AA}$ ) (it means that the efficient collision duration can actually be much longer than the time corresponding to a detuning of  $25 \text{ cm}^{-1}$ ), (e) integrated intensities of the water vapor lines are known nowadays with uncertainty, which is only slightly smaller than 1%, even by the most optimistic estimate, and absorption near the center of the strong lines exceeds the continuum one by many orders of magnitude.

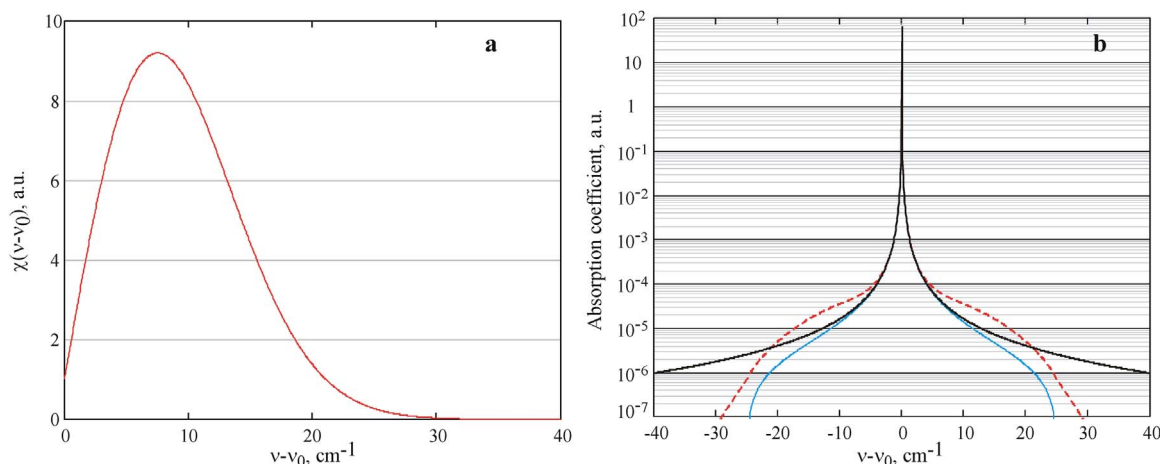
Allowing for the aforesaid, we constructed an empirical model, which is similar to (8) with the  $\chi$ -function that has the following form:

$$\chi(\nu - \nu_0) = \left( 1 + A \cdot \frac{|\nu - \nu_0|}{\Delta\nu_{\text{wing}}} \right) \cdot \exp\left( -\frac{(\nu - \nu_0)^2}{\Delta\nu_{\text{wing}}^2} \right). \quad (10)$$

It includes two variable parameters:  $A$ , which determines the wing amplitude and  $\Delta\nu_{\text{wing}}$  being the characteristic width of the wing. Fig. 1 shows the plot of this function and the shape of an isolated Lorentz line with and without allowance for the modified wing calculated using Eqs. (8)–(10).

This variation in the shape of the line (at such values of  $A$  and  $\Delta\nu_{\text{wing}}$ , which allow one to describe the observed excess continuum absorption) has almost no effect on its central part (the deviation from the Lorentz shape near the line center will be noticeable at the signal-to-noise ratio exceeding  $10^7$ ) and integrated intensity. A noticeable change in the absorption is observed in the region of the intermediate wings ( $5\text{--}20 \text{ cm}^{-1}$ ), and for great detuning values the decrease is faster compared with that of Lorentz curve.

It should be emphasized that the model presented makes no claims as to provide a rigorous description for all available experimental data in all spectral ranges. In particular, the  $\chi$ -function (10) was not adjusted to the continuum spectra in-between bands, because the integral continuum absorption in these spectral areas constitutes a small part of the total cross-section of the observed continuum. We deliberately used very simple form of the model with minimum number of parameters. However, it allows us to demonstrate that the excess continuum absorption, which is observed in three significantly different spectral regions, namely the rotational and fundamental ro-vibrational bands of the  $\text{H}_2\text{O}$  spectrum, can be described as a contribution from the intermediate wings of the lines. An accurate physically based model of the monomer line shape, which could be applicable to an arbitrary detuning from the line center, should allow for the specific intermolecular interaction potential and depend on the transition quantum numbers. At the present time, such a calculation is available only in the quasistatic approximation [46], which is valid when detuning from the line center is much greater than the



**Fig. 1.** Left (a):  $\chi$ -function calculated by Eq. (10) with the use of the parameters  $A=20$  and  $\Delta\nu_{\text{wing}}=11 \text{ cm}^{-1}$  as a function of the detuning frequency. Right (b): Lorentz profile with a half-width of  $5 \cdot 10^{-3} \text{ cm}^{-1}$  (150 MHz) (bold solid line); the same profile with the wings cut off at the  $\pm 25 \text{ cm}^{-1}$  detuning and the cut-off line “brought down” to the zero level (as in the CKD model) (thin solid line); the latter profile with the added wings, which are calculated by Eq. (8) using the  $\chi$ -function shown on the left is presented by the dashed line.

reversed duration of collision, i.e. for “very far” wings.

### 3. Description of the experimental spectra

Due to ambiguity of the nature of the continuum absorption, the commonly accepted convention is to determine the latter on the basis of the experimental data by subtracting the calculated contribution of the monomer lines from the total absorption observed in the experiment:

$$\alpha_c(\nu) = \alpha_{\text{total}}(\nu) - \sum_i R(\nu, \nu_i) \cdot S_i (f_{\text{line}}(\nu - \nu_i) + f_{\text{line}}(\nu + \nu_i)), \quad (11)$$

where  $\alpha_{\text{total}}(\nu)$  is the experimentally measured absorption, and  $f_{\text{line}}(\nu - \nu_i)$  is the shape of the monomer line without the far wings (e.g., using the “cutoff” at  $25 \text{ cm}^{-1}$ , as in Eq. (9)).

Herein, we follow convention (11) and interpret the water vapor continuum absorption using the model, which includes two components, namely, the dimer contribution (Eq. (7)) and the intermediate and far-wing contribution (Eqs. (8)–(10)):

$$\alpha_c(\nu) = \alpha_{\text{dimer}}(\nu) + C(\nu). \quad (12)$$

This model was used to describe the continuum in three regions, specifically: (1) the band near  $3600 \text{ cm}^{-1}$ , which corresponded to the fundamental stretching modes of the O–H bond; (2) the band near  $1600 \text{ cm}^{-1}$ , corresponding to the fundamental bending vibrational mode of the  $\text{H}_2\text{O}$  molecule; and (3) the rotational spectrum band in the range from 50 to  $200 \text{ cm}^{-1}$ .

Additionally, we tried to use the model to describe the  $\text{H}_2\text{O}$  continuum spectrum in the millimeter-wave range ( $6.3\text{--}8.6 \text{ cm}^{-1}$ ).

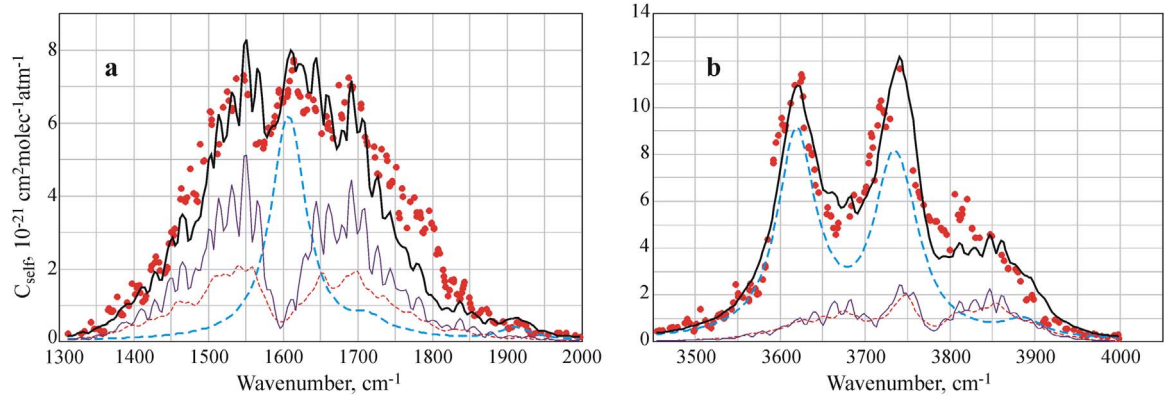
All the analyzed spectra of the continuum absorption are related to room temperature (295 K). They were recalculated in terms of units of the continuum coefficient,  $\text{cm}^2 \text{ molecule}^{-1} \text{ atm}^{-1}$ , which were used first by Burch [47] and are still in use. To calculate the monomer contribution using formula (11), we used the common line-by-line sum procedure. The line parameters (integrated intensity, width, and the central frequency) were taken from the HITRAN database [48]. The Voigt profile, whose wings were cut off at a detuning of  $25 \text{ cm}^{-1}$ , was used for the line profile  $f_{\text{line}}(\nu - \nu_i)$ , and the entire line was brought down to zero to ensure the spectrum continuity. Strictly speaking, this lowering results in a minor redistribution of the integrated absorption intensity from the resonance lines to the continuum. However, we used it because it does not impact the conclusions

made, but makes comparison with previous works more convenient. It is worth noting that using the Hartmann-Tran profile (HTP), which was recently recommended by the IUPAC [49] will have no impact on the retrieved continuum because the HTP differs from the Voigt profile only within several line widths from the line center.

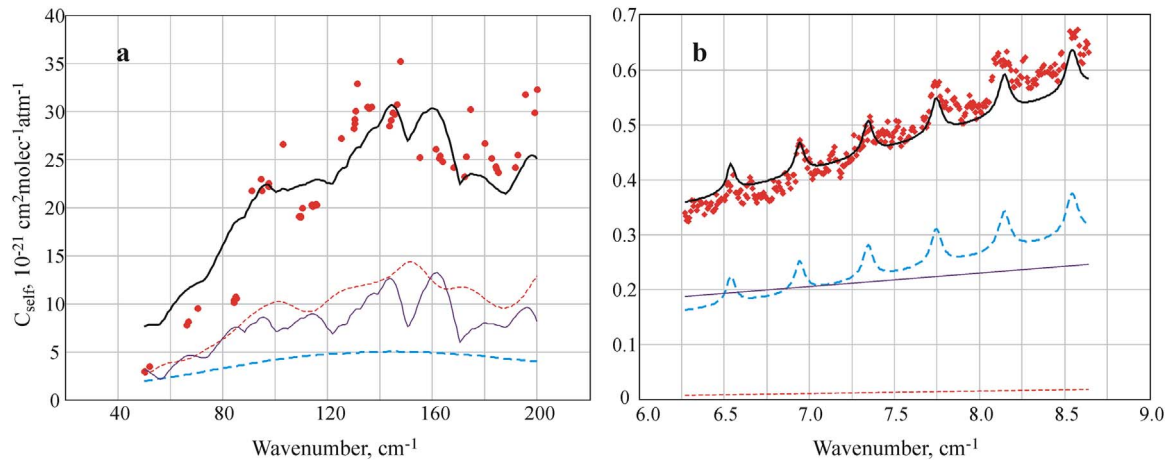
The first two spectra were taken from the paper by Ptashnik et al. [17]. The third spectrum was taken from the recent work by Odintsova et al. [31]. The millimeter-wave continuum spectrum is presented in the paper by Serov et al. [21].

The spectra of the bound dimers in the bands near  $3600$  and  $1600 \text{ cm}^{-1}$  were modeled by analogy with the work [17] though with certain different features. The first one is related to the modeling near  $3600 \text{ cm}^{-1}$ . The central frequency of the peak in the experimental spectrum of the continuum is located approximately  $20 \text{ cm}^{-1}$  higher than the corresponding vibrational mode of the dimer, which is known from the calculations on the basis of the perturbation theory [32] and from “cold” beam experiments [33,34]. This difference, in principle, can be due to redistribution of dimer line intensities in the spectrum at room temperature. So, the position of the absorption maximum in the band does not necessarily coincide with the corresponding mode frequency. One can also assume that the use of the Lorentz profile for modeling the shape of the ro-vibrational band of the dimer spectrum is an rather rough approximation. Despite this fact, the dimer nature of the peak in the spectrum of the water vapor continuum near  $3620 \text{ cm}^{-1}$  can be evidenced, in particular, by the stronger temperature dependence of absorption compared with that in the adjacent regions [17]. Since there are no theoretical data about the actual shape of the ro-vibrational bands in the dimer spectrum, we decided to shift the corresponding frequency in the dimer spectrum model to make the experimental spectrum description using the simplified model more accurate. The second difference is that we chose a slightly different width of the dimer bands, specifically,  $54 \text{ cm}^{-1}$ , since a better agreement of the model with the experimental data was achieved in this case.

To evaluate the contribution from metastable dimers, also by analogy with [17] we used the normalized spectrum of the monomer (calculated as explained above but the line wings were cut off at  $200 \text{ cm}^{-1}$ ) doubled and broadened homogeneously by the characteristic lifetime of the metastable state (HWHM of all lines was assumed to be equal to  $10 \text{ cm}^{-1}$ ). The difference from the aforementioned work is in that the number density of metastable dimers was determined according to Eqs. (4)–(6) from the



**Fig. 2.** Experimental spectra of the water vapor continuum bands at  $1600\text{ cm}^{-1}$  (a) and  $3600\text{ cm}^{-1}$  (b) from the paper [17] approximated by the model including the contribution from the water dimers and the empirically calculated contribution from the line wings. The dots are the experimental data, the bold solid curve represents the model, the bold dashed curve, the thin dashed curve, and the thin solid curve are the contributions from the bound dimers, metastable dimers, and line wings, respectively. The contribution from the line wings is calculated using Eqs. (8)–(10).  $A=32$  for the  $1600\text{ cm}^{-1}$  band and  $18.5$  for the  $3600\text{ cm}^{-1}$  band,  $\Delta\nu_{\text{wing}}=11\text{ cm}^{-1}$  for the both bands.



**Fig. 3.** Experimental spectra of the  $\text{H}_2\text{O}$  continuum in far infrared [31] (a) and millimeter-wave [21] (b) ranges approximated by the model allowing for the contribution from the water dimers and the empirically calculated contribution from the line wings. The dots are the experimental data, the bold solid curve represents the model, the bold dashed curve, the thin dashed curve, and the thin solid curve are the contributions from the bound dimers, metastable dimers, and line wings, respectively. The contribution from the line wings calculated by using Eqs. (8)–(10).  $A=14$  and  $215$  for the left-hand and right-hand panels, respectively, and  $\Delta\nu_{\text{wing}}=11\text{ cm}^{-1}$  in both cases.

second virial coefficient and the constant of dimerization of the bound dimers.

Optimal modeling of all spectra was achieved by setting the parameter  $\Delta\nu_{\text{wing}}$  to  $11\text{ cm}^{-1}$ . The value of the parameter  $A$  for each spectrum was determined by fitting. By contrast with the CKD model, the considered model of the line wing at such of  $\Delta\nu_{\text{wing}}$  is characterized by a significantly faster decrease with growing detuning. Therefore, in the frame of common terminology one can assume that this model corresponds to the predominant contribution from the intermediate wings of resonant lines. The results of modeling the continuum in the  $3600$  and  $1600\text{ cm}^{-1}$  bands are presented in Fig. 2.

It should be noted that in general, the quality of describing the spectra using the proposed model is very similar to that presented in the paper [17] since the contribution from the modified wings looks fairly identical to the strongly broadened monomer spectrum. However, unlike the estimations in which the entire continuum was attributed to the water dimers [17], our estimations show that the integrated contributions from the bound and metastable dimers are about 80% and 50% for the bands near  $3600$  and  $1600\text{ cm}^{-1}$ , respectively. Presumably, the rest is contributed by the monomer intermediate line wings.

Note that typical uncertainty of the integral intensities of the bound dimer bands can be estimated as 20% [34]. Definitely, such

uncertainty can influence the particular values of the coefficients in the model of the continuum. However, this change will be quantitative rather than qualitative. For example, simultaneous increasing of all bound dimer bands intensity by 20% increases the total dimeric contribution to about 90% and 60% for the bands near  $3600$  and  $1600\text{ cm}^{-1}$ , respectively. Moreover, as it is shown in Fig. 2, the bound dimer spectra in the fundamental ro-vibrational bands have a different shape of the envelope compared with the contribution from the super-Lorentzian wings of the monomer lines. Thus, these two kinds of absorption can be easily distinguished.

To model the absorption spectrum of the bound dimers in the  $50\text{--}200\text{ cm}^{-1}$  range, we used the results of the *ab initio* calculations [29]. The spectrum shown in Fig. 10 of the paper [29] for  $298\text{ K}$  was recalculated for a temperature of  $295\text{ K}$  using Eq. (26) from the later work [39]. Additionally, we used the correction term  $\exp(\Delta D_0/kT)$ , which was mentioned in Section 1. The result of fitting our model (6)–(8) to the continuum in this range is shown in Fig. 3a. The integrated contribution of the bound and metastable dimers to the continuum was found to be about 64% in this frequency range. We admit that intensity of the bound dimer spectrum calculated in [29] can be underestimated. To attribute the observed continuum to dimers one should admit the underestimation factor of about 3, which seems very unlikely taking into

account the aforementioned agreement of the spectrum from [29] with the other calculations and experimental studies.

In the millimeter-wave range, we used the simplified model of the bound dimer spectrum [50], which was also based on the results of the *ab initio* calculation [29]. The parameters of the model were chosen to achieve the best correspondence with the experimentally obtained dimer spectra [21]. The contribution of metastable dimers was estimated as the doubled and strongly broadened monomer spectrum. The remaining continuum was described by our line wings model (8)–(10) as shown in Fig. 3b.

It turned out that to describe the observed continuum in the latter case, the parameter  $A$  should be an order of magnitude greater than that for other ranges. This discrepancy was not unexpected, since in this case, which corresponds to the low edge of the rotation band, inaccuracy of estimating the contribution from the intermediate wings of monomer lines as well as from the quasibound dimers significantly affects the result. This is easily understood by analogy with analysis of description of the dimer ro-vibrational band by the Lorentz profile: upon the whole, a qualitatively good description can be obtained for the entire band, which fills a certain spectral region continuously and in a hill-shaped manner, but one cannot expect good agreement with the simplified model in the narrow part of this region and especially at its edges. Inadequacy of the model of the metastable-dimer spectrum in this range manifests itself, in particular, in poor correspondence between the frequency dependencies of the model and experimental spectra, which can be seen in Fig. 3b. Moreover, due to the radiation term (Eq. (8)), the contribution from the line wings becomes almost an order of magnitude smaller, which requires the corresponding increase in the wings amplitude. Thus, in our opinion, the disagreement in the millimeter wave range does not disprove the general character of the model proposed.

It should be noted that in the millimeter-wave range, the spectrum of the stable dimer is studied much better than that in other bands. Therefore, thorough investigation of the temperature dependence of the excess continuum in this band seems to be preferable for clarifying further the possible nature of this absorption.

Despite the significant difference in the parameter  $A$  values, the total contributions from the bound and metastable dimers in the 6.3–8.6 and 50–200  $\text{cm}^{-1}$  ranges are almost the same amounting to 54% and 64%, respectively (allowing for all inaccuracies and approximations of the models, one can state that they coincide within the uncertainties), which indicates the common nature of the excess continuum in these two frequency ranges.

#### 4. Discussion

Generalizing the above-presented results, one can on the whole conclude that the proposed empirical model describes fairly well the excess continuum absorption, which amounts to 20–50% of the observed continuum. The amplitude coefficient  $A$  does not vary significantly over the considered spectral range (excluding the millimeter-wave range discussed above). Deviations of the obtained values of  $A$  do not exceed 50% from the mean value. It can be explained not only by the approximate character of the models used (for example, we completely ignore the rotational state dependence of intermediate line wing shape in spite of the known fact that collisional broadening can vary by a factor of 2 or more within the band) but also by uncertainties in shape and intensity of the dimer bands, which differ from band to band. Nevertheless, the estimates made allow us to assume with high probability that the observed excess continuum absorption is objective reality, which can be explained by a variation in the profile of the line wing. The absolute modification of the profile at certain detuning

from the line center reaches a factor of 10 (Fig. 1). However, because of quite a large value of the detuning this variation is smaller than the line amplitude by many orders of magnitude, and its relative contribution to the integrated intensity amounts to a small value of an order of 0.001, which is much smaller than the uncertainty with which the intensities of the resonance lines are known. The monomolecular nature of the excess continuum is also indirectly confirmed by its spectral heterogeneity. The dimeric absorption (a tremendous number of collisionally-broadened lines, which are more or less uniformly spread over the range) is very smooth. The spectrum of free-pairs is even smoother due to the very short collision time causing the absorption. Therefore the heterogeneity of the spectrum is the evidence that it belongs to the monomer line wings. A similar non-monotonicity of the water continuum, which is comparable with its measurement error in each separate transparency window, can be found in all wideband studies [17,31,51].

In Sections 1 and 2, we mentioned that the proposed empirical model of the intermediate line wings should not be considered as a predictive one. It counts in a favor of the correctness of our general approach to interpretation of the water vapor continuum within the rotational and fundamental ro-vibrational bands. Consideration of the spectra corresponding to the wings of those bands and to the transparency windows between them was left beyond the scope of the present paper. We estimated roughly the integral contribution of the continuum spectra within the aforementioned regions to the total continuum absorption using the MT\_CKD model, which is in reasonable general agreement with the available experimental data [37]. Such estimations showed that the integral intensities corresponding to the in-between band ranges (2000–3450  $\text{cm}^{-1}$  and 4000–5000  $\text{cm}^{-1}$ ) amount to only about 3% of integral intensities within the spectral regions shown in Fig. 2 (1350–2000  $\text{cm}^{-1}$  and 3450–4000  $\text{cm}^{-1}$ ). Thus, the conclusions made in this work are based on consideration of the major part (97%) of the observed water vapor continuum in the fundamental ro-vibrational bands.

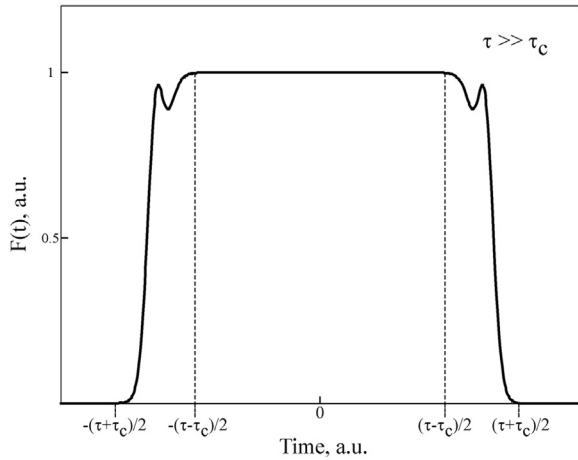
In terms of the line profile, the essence of our hypothesis is that the real resonance line is “Lorentzian”, “super-Lorentzian” and “sub-Lorentzian” in the regions of the near, intermediate, and far wings, respectively. Let us analyze the validity of this hypothesis. The sub-Lorentzian behavior in the region of the far wings became evident long ago from the analysis of the experimentally observed absorption in the wings of the  $\text{CO}_2$  bands [52]. Theoretical calculations concerning the shape of the far wings can be found, e.g., in the papers [16] and [53], and the references therein. In particular, it was shown that the exponential decay of the far wing is related to the finite time interval of a molecular collision. In water vapor the sub-Lorentzian behavior is confirmed by agreement of the empirical MT\_CKD model with the experimental observations of the continuum in transparency windows [37]. This effect can be demonstrated using the simple classical model.

Let us consider the molecule-oscillator, which interacts with an external harmonic force (electromagnetic wave) during the time period  $\tau$ :

$$\ddot{x} + \omega_0^2 x = F(t) \cdot \cos \omega t, \quad (13)$$

where  $\omega_0$  is the angular eigenfrequency of the oscillator, and  $\omega$  is the angular frequency of the external force. Let  $F(t)=1$ , if  $-\tau/2 \leq t \leq \tau/2$ , and  $F(t)=0$  for all other values of the argument. Such a model corresponds to the case of instantaneous collisions with the inter-collision interval equal to  $\tau$ . The energy received by the oscillator from the external force, can be calculated using the following formula [54] (the constant term is omitted):





**Fig. 4.** Profile of the function  $F(t)$  from Eq. (17) (without preserving the scale of the time axis), at which the wing of the resonance line lies above the wing of the Lorentz line within a certain frequency range corresponding to the intermediate line wings.

$$\Delta W = \frac{1}{2} \left| \int_{-\tau/2}^{\tau/2} F(t) \cos \omega t \cdot e^{-i\omega_0 t} dt \right|^2. \quad (14)$$

For the above-specified function  $F(t)$ , we have:

$$\begin{aligned} \Delta W &= \frac{1}{2} \left| \frac{1}{2} \int_{-\tau/2}^{\tau/2} \left( e^{i(\omega - \omega_0)t} + e^{-i(\omega + \omega_0)t} \right) dt \right|^2 \\ &= \frac{1}{2} \left( \frac{\sin^2 \frac{(\omega - \omega_0)\tau}{2}}{(\omega - \omega_0)^2} + \frac{\sin^2 \frac{(\omega + \omega_0)\tau}{2}}{(\omega + \omega_0)^2} + \frac{\cos \omega_0 \tau - \cos \omega \tau}{\omega^2 - \omega_0^2} \right) \end{aligned} \quad (15)$$

For the energy received by the equilibrium gas of such molecule-oscillators, this formula should be averaged allowing for the exponential function of time distribution between the collisions:

$$\begin{aligned} \Delta \bar{W} &= \frac{1}{\tau_0} \int_0^\infty \Delta W \exp\left(-\frac{\tau}{\tau_0}\right) d\tau \approx \frac{1}{4} \\ &\cdot \left( \frac{1}{(\omega - \omega_0)^2 + 1/\tau_0^2} + \frac{1}{(\omega + \omega_0)^2 + 1/\tau_0^2} \right), \end{aligned} \quad (16)$$

where  $\tau_0$  is the mean inter-collision time. Formula (16) is valid if  $1/\tau_0 \ll \omega_0$ , or, in other words, if the line width is much smaller than its central frequency, which is almost always fulfilled under the usual spectroscopy conditions. Thus, in the case of instantaneous collisions of the gas molecules we obtain the classical line shape which is long known from the works of Lorentz and Van Vleck and Weisskopf.

For the case of smooth “switching-on” and “switching-off” of the oscillator interaction with an external force, the calculations using formulas (14) and (16) lead to a steeper descending shape of the line far wings, and the descent rate depends on the smoothness degree of the function  $F(t)$ . For example, if the external force “switches on and off” according to the linear law, the far line wing behaves as  $\sim 1/(\omega - \omega_0)^4$ , whereas, if the switching-on/off function is hyperbolic tangent, the decrease becomes exponential. The latter seems to be closer to reality. This means that the resonance line absorption is rather well localized in the spectral region. Formally, the exponentially decreasing wing is infinite, as well as the Lorentzian one, but its contribution to absorption at large detunings off the center is negligibly small.

The reason for the super-Lorentzian behavior is less obvious. As it is stated in [55]: “the super-Lorentzian line shape in the intermediate wing region was not supported by any known physics.” However, such a behavior can easily be explained even in the

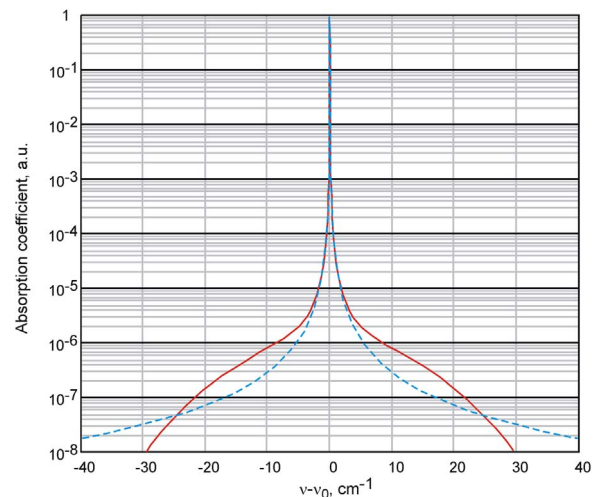
framework of the above-mentioned molecule-oscillator model. To do this, let us assume that the external force turns on and off with oscillations, rather than monotonously. In the case of water vapor, such oscillations can arise due to rotation of the colliding molecules. The characteristic profile of the function  $F(t)$ , which would qualitatively reproduce the empirical profile shown by the dashed line in Fig. 1b, is represented in Fig. 4. Note that only the presence of oscillations is of basic importance. The specific shape of the function  $F(t)$ , although affecting the final result, is chosen in this work to simplify its mathematical representation:

$$\begin{aligned} F(t) &= \frac{1}{2} \left( \tanh\left(\frac{4t + 2\tau}{\tau_c}\right) - \tanh\left(\frac{4t - 2\tau}{\tau_c}\right) \right) + \frac{A_0}{2} \left( \exp\left(-\frac{16(t - \tau/2)^2}{\tau_c^2}\right) \right. \\ &\quad \cdot \sin^2\left(\frac{2\pi t}{T_0} - 2\pi a\right) + \exp\left(-\frac{16(t + \tau/2)^2}{\tau_c^2}\right) \cdot \sin^2\left(\frac{2\pi t}{T_0} + 2\pi a\right) \left. \right) \end{aligned} \quad (17)$$

This function depends on the following parameters:  $\tau$  is the time interval between two successive collisions of a molecule,  $\tau_c$  is the duration of the function  $F(t)$  turning “on/off”, which corresponds to duration of the molecular collision process,  $A_0$  is the amplitude of oscillations during the transition process, and  $T_0$  and  $a$  are the period and initial phase of these oscillations, respectively.

Using function (17) in the molecule-oscillator model (13), we can obtain the line shape which is almost identical to the empirical model (Fig. 1b). The following parameters were used:  $\omega_0 = 2\pi \cdot 3 \times 10^{12} \text{ s}^{-1}$  and  $\tau_0 = 10^{-9} \text{ s}$ , which corresponds to the line in pure water vapor in the range of maximum intensity of the rotation spectrum with the central frequency  $\nu_0 = 100 \text{ cm}^{-1}$  and a half-width of 160 MHz,  $\tau_c = 1.5 \times 10^{-12} \text{ s}$ ,  $T_0 = 6 \times 10^{-12} \text{ s}$ ,  $A_0 = 3$  and  $a = 0.24$  (the line shape calculated after the averaging in accordance with the exponential function of the time distribution between the collisions does not depend on  $a$ ). Fig. 5 shows the calculated line profile along with the corresponding Lorentz profile. The specified time  $\tau_c$  approximately corresponds to the characteristic collision duration of the Ar-CO<sub>2</sub> molecules calculated at a temperature of 240 K [15]. Allowing for a lower molecular mass of water, the characteristic time should be shorter. However, due to the dipole moment, the H<sub>2</sub>O molecules “feel” each other at a significantly longer distance, which should considerably increase the interaction time.

It follows from the performed calculations that within a certain range of the frequency detuning off the line center, which depends on the specific characteristic of the colliding molecular pair and the collision itself, the line wing is above the Lorentz one.

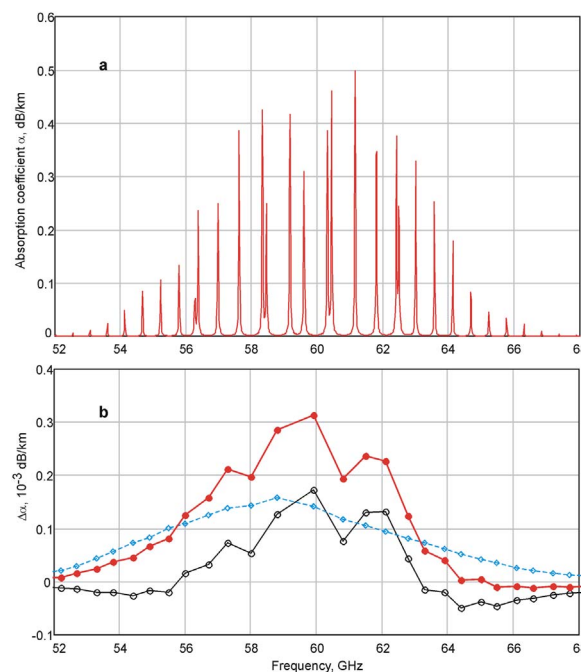


**Fig. 5.** Profile of the resonance line calculated by solving Eq. (13) using the functions  $F(t)$  from (17) with the parameters specified in the text (solid line). The dashed line is the Lorentz profile.

When choosing the unknown parameters  $\tau_c$ ,  $T_0$ , and  $A_0$ , we based our choice on the idea that the resulting spectrum should approximately look like that obtained from empirical modeling (Sections 2 and 3). This allows one to make conclusions about the possible nature of oscillations and, consequently, the super-Lorentzian behavior of the line wing. An increase in the absorption in the line wing occurs for the detuning equal to the oscillation frequency. Period  $T_0 = 6 \times 10^{-12}$  s corresponds to detuning of about  $6 \text{ cm}^{-1}$  from the line center. The specified oscillation frequency is more than an order of magnitude lower than the average molecule rotation frequency ( $\sim 200 \text{ cm}^{-1}$ ). So it is due to the type of differential rotational effect rather than the relative molecular rotation itself. It can correspond, e.g., to the well-known effect of the so-called “rotational resonance” [56]. The essence of the effect is that the molecules in the identical states interact with each other resonantly, i.e., stronger than upon the average. The effect manifests itself in the dependence of the collision cross-section on the rotational quantum number. This dependence has the general monotonous decrease. However, it also has a kind of the maximum corresponding to such a state, in which the absorbing molecule interacts resonantly with the greatest number of the surrounding molecules. (This characteristic dependence manifests itself clearly, e.g., in the case of the self-broadening of the lines in the regular spectrum of the polar OSC molecule [57]).

Possibility of a non-monotonic transient process (very similar to that shown in Fig. 4), which occurs during the molecular collision in real gases is confirmed by the result of calculation of the relaxation matrix elements presented in Fig. II.C1 on p. 51 of the book by Hartmann et al. [58]. This similarity can be regarded as a validity confirmation of our hypothesis.

Another possible explanation for “uplifting” of the line wing above the Lorentz one should be mentioned. It is well known that the approximation of independence of the molecular oscillators is valid only with certain limitations. Therefore, even in the framework of the impact approximation one can make an example, when the line wing is located above the Lorentz one. Within the first approximation, the effect of the collisional coupling of the lines (which is also known as the line mixing or line interference effect or spectral exchange), leads to “uplifting” of a line wing above the Lorentz one. The effect also influences the band shape as a whole, specifically, it increases absorption in the central part and decreases it at the band periphery, i.e., the effect manifestation is qualitatively similar to the behavior of the observed continuum absorption. To demonstrate the possible manifestation of the line coupling effect, we consider the absorption band of oxygen near 60 GHz ( $2 \text{ cm}^{-1}$ ), where this effect manifests itself strongly due to the specific features of the  $\text{O}_2$  molecule even under the atmospheric conditions and is well studied [59]. The band includes several tens of the intensity-significant (under usual conditions) lines, whose central frequencies are located in the range 50–70 GHz. To qualitatively analyze the influence of the effect on the band profile, it is sufficient to use the simplest model of the line profile, which makes it possible to allow for the collisional coupling of the lines in the first order of pressure [60] and the known line parameters [61]. The pressure can be chosen so as to make the lines in the spectrum look isolated. In such a spectrum the “continuum” was found in accordance with Eq. (11) using the classical profile of the isolated resonance line. For the sake of demonstration, we choose the cutoff frequency smaller than the aforementioned  $25 \text{ cm}^{-1}$  but large enough to make the ratio  $\nu_{\text{cut}}/\Delta\nu_i$  sufficiently great (more than 100). The upper panel of Fig. 6 shows the calculated spectrum of the absorption coefficient in pure oxygen under a pressure of 10 mbar. The panel below demonstrate the continuum obtained by the same method, which is traditionally used when the water vapor continuum is measured, namely, at the points corresponding to the deepest “transparency



**Fig. 6.** a) Absorption in the 60-GHz oxygen band, which is calculated using the model [60,61] allowing for the collisional line coupling. The absorption is calculated for pure oxygen under a pressure of 10 mbar. b) Correction to the absorption in the band: thin solid black line represents the correction caused by the influence of the collisional line coupling, thin dashed blue line is the correction due to cutting off of the line wings and setting the line profiles down, and thick solid red line is the total correction. The corrections are calculated in the transparency microwindows (see the text for the details). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

microwindows” between the lines (in our case, only the microwindows with absorption below  $2 \cdot 10^{-3} \text{ dB/km}$  were used). In this hypothetical case, the obtained “continuum” can easily be subdivided into two parts shown in Fig. 6. They are the part originated from the collisional line coupling, which corresponds to the difference between the absorption models with and without allowance for the collisional coupling (Fig. 6, thin solid line), and the part, which corresponds to cutting-off of the line wings and setting their profiles down (Fig. 6, thin dashed line). The spectrum of the “continuum” obtained in this way has much in common with the observed water vapor continuum: (a) its profile resembles the envelope of the absorption band, (b) its value is several orders of magnitude lower than absorption at the resonance lines maxima, and, which is most important, (c) its value is proportional to the squared pressure. Moreover, the common factor is also that the frequency dependence of the continuum is not smooth as discussed above. In the oxygen case, since the band spectrum is very similar to the equidistant one, it is mainly related to the different value of the line coupling.

The lines in the rotational and ro-vibrational spectra of the water vapor are not isolated either. It is known, that the effect of collisional coupling is negligibly small within the impact approximation for most water vapor lines [62]. Nevertheless, the situation can be different beyond the impact approximation. The model allowing for both the finite duration of collisions and the line mixing effect for the water vapor continuum within the quasistatic approximation (very far wings) was suggested [46,63]. In the case where neither the impact nor quasistatic approximations are valid (for intermediate wings), the influence of the line mixing effect have not been evaluated so far. No thorough analysis of how the line mixing can affect the continuum obtained by Eq. (11) in the region of the close and intermediate wings has been performed.

The analogy of the ro-vibrational spectrum of water vapor with

the oxygen fine-structure band cannot be regarded as strict. It is considered to be only an example of an unaccounted physical effect, which can influence the shape of the spectrum of monomolecular absorption in water vapor.

To conclude, it should be noted that the considered correction of absorption in the line wing, which is required for describing the excess continuum absorption, is equal to only about  $10^{-6}$  of the absorption at the maxima of the resonance lines (see Fig. 1). The ratio between the continuum absorption and the maximum resonance absorption, e.g., at the center of the rotational band of  $\text{H}_2\text{O}$ , is approximately the same. At such a level, the influence of the above-mentioned and, possible, some other effects cannot be excluded.

The well-known fact that the temperature dependencies of different continuum components differ should also be mentioned. Therefore, we believe that studies of the excess continuum at various temperatures are currently the most promising for advancing the understanding of its nature.

## 5. Conclusion

Thus, making no claims as to developing a new, physically based model of the line shape, we identify the problem of existence of the excess continuum absorption in the three main bands of the water vapor spectrum. The analysis presented allowed us to single out the most probable reason for this absorption and indicate the necessity of developing a more accurate model for the shape of the resonance lines of water vapor in the region of intermediate and far wings, compared with that used in the current radiation propagation models. Development of such a model will make it possible to finally get rid of ambiguity of the empirical notion of the “continuum” (Eq. (11)). It will be possible to determine the total absorption as an almost independent sum of the monomolecular (including resonance part of monomer lines as well as their intermediate and far wings calculated taking into account details of collisional interaction) and bimolecular absorption arising as an additional absorption mechanism resulting from the collisional interaction. If necessary, the approach can be easily extended by similar way to the general case of multimolecular interactions until the series expansions (1) and (2) converge.

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