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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.

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–Khintchine 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:

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

where p is the gas pressure, ρ 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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$$\alpha(\nu) = \alpha_1(\nu)\cdot\rho + \alpha_2(\nu)\cdot\rho^2 + \alpha_3(\nu)\cdot\rho^3 + \ \ldots, \qquad (2)$$

where ν is the frequency and α_1, α_2, α_3… 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 Loretzians. 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 π 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 quasibound 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, π 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 8.9×10^{-4} and 2.3×10^{-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_2O 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