



The water dimer millimeter-wave spectrum at ambient conditions: A simple model for practical applications



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ABSTRACT

A simple model of the water dimer millimeter-wave spectrum at pressures and temperatures typical of Earth's atmosphere is proposed. The model is based on high accuracy *ab initio* calculations and is supported by experimental observations of the dimer spectrum in cold molecular beams. It is demonstrated that the model corresponds to the spectra calculated *ab initio* and recorded at room temperature. The model is used for assessing atmospheric brightness temperature variations caused by the water dimer absorption. A possibility of direct radiometric observation of the dimer in the Earth's atmosphere is shown.

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1. Introduction

The water dimer (H₂O)₂ is known to be a hard-to-detect atmospheric species that affects Earth's radiation balance and climate [1–4], homogeneous condensation [5], and atmospheric chemistry [6]. Despite decades of studies and considerable experimental efforts there were no secure direct observations of water dimers in equilibrium at environmentally relevant temperatures, either in the atmosphere or in laboratory until the year of 2013, when unambiguous observation of the dimer spectrum in equilibrium water vapor at room temperature was reported [7]. A sequence of four peaks corresponding to the dimer end-over-end rotation was detected near the resonator spectrometer sensitivity threshold [8] in the 105–150 GHz range. Further experiments resulted in observation of more intense continuation of this sequence. Six more dimer peaks were registered in the 190–260 GHz range [9]. Taken together, the earlier extensive theoretical and experimental studies of the water dimer and the observation of its spectrum

at ambient conditions offer encouraging signs that this new technique will be a useful tool to get a deep insight into the Earth's radiation balance and the contribution of water to atmospheric processes.

However, the dimer spectrum is so dense and complicated that usual spectroscopic methods based on individual line or band shape analysis are not applicable for extracting quantitative data about the dimer abundance from experimental recordings. The most accurate *ab initio* approach to calculating the dimer spectrum reported in the work [10] gives a qualitative picture of the spectrum but cannot be directly used for fitting for the following reasons: (i) insufficient accuracy of the frequency scale and (ii) use of the symmetric top approximation in the calculations, which may result in discrepancies with the real spectrum. Moreover, there is the long recognized problem of separating the true bound dimer spectrum from other components of bimolecular absorption [11], as well as from the somewhat uncertain contribution coming from the far wings of the monomer lines.

The main goal of this work is the development of a model based on *ab initio* calculations that would allow solving the aforementioned problems and could easily be fitted to experimental spectra recorded in a broad range of

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pressures and temperatures related to Earth's atmospheric conditions.

Details of the model development are given in Section 2. The agreement of the model with the water dimer experimental spectra observed at room temperature is demonstrated in Section 3. Section 4 gives an example of using the model for assessing the possibility of direct detection of the water dimer in the atmosphere by means of available microwave radiometers.

2. Model

Ab initio calculations of the high resolution water dimer spectrum in the millimeter and far infrared domain at temperatures in the interval 250–330 K were previously reported by Scribano and Leforestier [10]. These calculations rely on the explicit consideration of all possible transitions within the entire rovibrational bound state manifold of the dimer. The water dimer is a highly nonrigid, near prolate top molecule that undergoes several simultaneous tunneling motions and has six low frequency intermolecular vibrational modes. Four of these modes are located below 200 cm^{-1} resulting in thousands of vibrational states populated at ambient temperature. The dimer is described in the calculations by the flexible 12-dimensional potential energy surface previously fitted to the observed far IR transitions [12]. The same surface was used for calculating the dimer equilibrium constant $K_p(T)$ [13], which determines the partial pressure of the dimer in water vapor and, therefore, the overall intensity of the dimer spectrum. Understanding of the spectrum structure used in the calculations was based on the symmetric-top approximation and derived from the previous extensive theoretical and cold molecular beam experimental studies performed by Saykally and collaborators [14].

The entire spectrum of the dimer may be divided into two essentially different components corresponding to: (i) the transitions between the levels of *A* and *B* type symmetries with irregular spectral patterns (this part hereafter will be called *A+B* spectrum) and (ii) the transitions between levels with E_1 symmetry (this part will be called *E* spectrum); this second component includes significant regular transitions corresponding to $J+1 \leftarrow J$, *K* lines, each fixed *K* series of which follows the quasi-rigid rotor spectral pattern. In the pressure range corresponding to typical partial pressures of water vapor in ambient atmosphere the first group of transitions forms a quasi-continuum absorption spectrum, whereas the second group of transitions results in the clear quasi-periodical sequence of resolved spectral features. This sequence of discrete lines is the unmistakable characteristic spectral label of the water dimer.

Fig. 1 presents typical *ab initio* spectra of the dimer calculated separately for *A+B* and *E* components at two different temperature and pressure conditions which were used in this work for the development of the model. For the pressure broadening of individual dimer lines a value of 30 MHz/Torr was adopted following the estimation given by Krupnov et al. [15]. The figure demonstrates in particular that the amplitude of the peaks in the *E* spectrum can be considerably enhanced by increasing the total pressure of water vapor, which results in a squared increase of the dimer

concentration. However, the peak contrast relative to the continuum background is decreasing.

It was demonstrated in our earlier work [15] that the peaks in the total absorption spectrum of the dimer are discernable only in the low frequency part of the spectrum. Inhomogeneous broadening of the peaks increases with frequency and the regular sequence turns into a noise pattern above ~ 350 GHz. Observation of characteristic dimer features above 350 GHz also becomes problematic due to the increasing contribution of strong monomer lines. On the other hand, a careful examination of the lowest part of the dimer spectra revealed that the rotational peaks become almost indistinguishable from the remaining absorption which looks like a continuum below ~ 60 GHz (Fig. 2). For these reasons we will limit our model of the dimer spectrum to the 60–350 GHz frequency range. However, *ab initio* calculated spectra will be shown in a broader range for clarity of the modeling problems.

At a given temperature the *A+B* spectrum can be approximately modeled using a simple monomial function:

$$\alpha_{AB}(\nu) = C_{AB}\nu^2, \quad (1)$$

where ν is a frequency and C_{AB} a constant. The quality of such an approximation is shown in Fig. 3, which demonstrates that in the range up to 350 GHz the function (1) is in reasonable agreement with the calculated spectrum.

For modeling the *E* spectrum using a similar monomial it is also necessary to take the peaks into account. It turned out that their shape can be satisfactorily approximated by a Lorentzian profile. So the *E* spectrum absorption can be modeled as

$$\alpha_E(\nu) = C_E\nu^2 + \sum_J \frac{I_J\gamma_J}{(\nu - \delta_J)^2 + \gamma_J^2}, \quad (2)$$

where C_E is a constant, I_J , γ_J and δ_J are respectively the amplitude, width and central frequency of the peak corresponding to the $J+1 \leftarrow J$ rotational transitions of the dimer.

The parameters of individual Lorentzian profiles in the range up to 350 GHz were determined from the *E ab initio* spectrum calculated for 296 K and for a water vapor pressure of 13 Torr. We then fitted simple empirical functions to the obtained values, which resulted in the following expression

$$I_J = 6.3 \times 10^{-11} J^4 \exp(-0.0872J) \quad (3)$$

for the dimer peak amplitudes giving absorption in cm^{-1} and

$$\delta_J = 11.239(J+1) + 8.68 \times 10^{-9}(J+1)^5 \quad (4)$$

for the peak central frequencies in GHz.

It was assumed that, within some reasonable pressure limits, the peak widths can be considered to consist of two components: (i) an inhomogeneous one that is determined by the spread of individual lines and is, therefore, constant and (ii) an homogeneous component which varies with pressure thereby determining the pressure broadening of the spectrum. So for modeling the peak width, the following

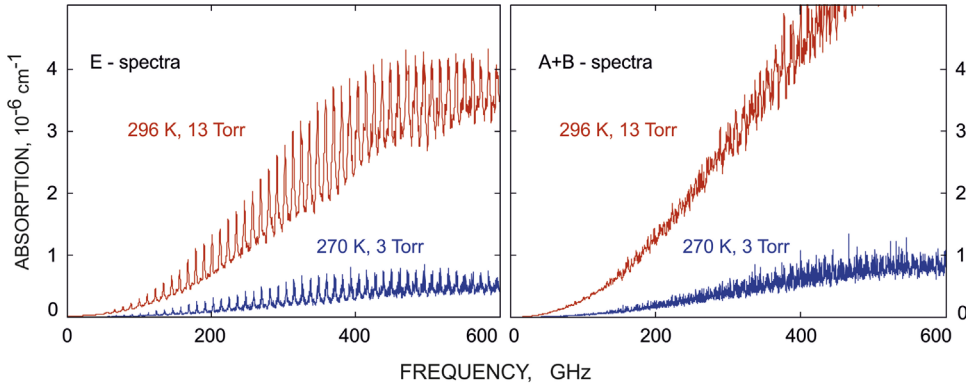


Fig. 1. Water dimer *ab initio* spectra corresponding to *E*-type transitions (left) and *A* plus *B* type transitions (right) at two different conditions calculated assuming a pressure broadening of 30 MHz/Torr.

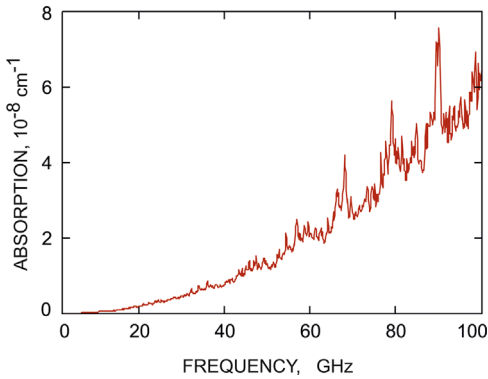


Fig. 2. Lowest frequency part of the total absorption spectrum of water dimer at 270 K and 3 Torr of water pressure.

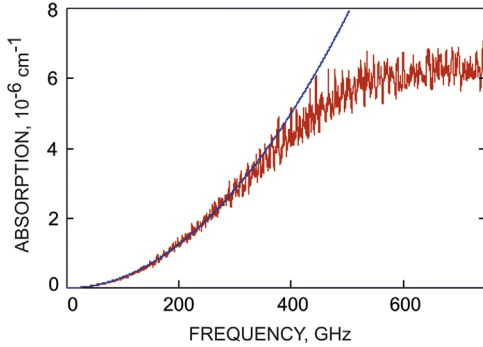


Fig. 3. Modeling of the *A+B* spectrum of the dimer at 296 K and 13 Torr by function (Eq. (1)) with $C_{AB}=3.13 \times 10^{-11} \text{ cm}^{-1}/\text{GHz}^2$.

expression in units of GHz was obtained:

$$\gamma_J = (0.108J - 4.43 \times 10^{-5}J^3) + 0.03(P - 13), \quad (5)$$

where P is the total pressure of water vapor in Torr.

The value of the C_E parameter determined from the same spectrum is $1.1 \times 10^{-11} \text{ cm}^{-1}/\text{GHz}^{-2}$.

Fig. 4 illustrates the very good agreement of the model with the calculated spectrum.

The model absorption for different temperatures and pressures can be recalculated using the empirical power

laws $(T/T_0)^{x_1}$ and $(P/P_0)^{x_2}$, with $x_1 = 10.67$ determined in an earlier work [10] and $x_2 = 2$ (bimolecular origin of the absorption). Thus, the total dimer absorption at given pressure and temperature can be approximated by

$$\alpha(P, T) = (\alpha_E + \alpha_{AB}) \left(\frac{T_0}{T} \right)^{10.67} \left(\frac{P}{P_0} \right)^2, \quad (6)$$

where $T_0 = 296 \text{ K}$ and $P_0 = 13 \text{ Torr}$. However, the above x_1 value, associated with temperature dependence, was determined for conditions where all spectral features of the dimer were smoothed by considerable pressure broadening. It thus encompasses the temperature dependence of both the equilibrium constant and of the two different components (*A+B* and *E*) of the dimer spectrum. Modeling the spectrum peculiarities henceforth required a separate determination of these dependences for each component of the spectrum. A reasonable agreement between calculated and model spectra was obtained with additional temperature exponent values of -0.4 , -2.3 and $+2.8$ for the *A+B* part, for the continuum part of the *E* spectrum, and for the sum of Lorentzians respectively. At the final step of our model construction, the parts of *A+B* and *E* spectra that look like continuum were combined in a single expression and the following equation for the total absorption in unit of cm^{-1} was obtained:

$$\alpha(\nu, T, P) = \left[4.29 \times 10^{-11} \nu^2 \left(\frac{T_0}{T} \right)^{-3.8} + \sum_j \frac{I_j \gamma_j}{(\nu - \delta_j)^2 + \gamma_j^2} \right] \left(\frac{T_0}{T} \right)^{13.5} \left(\frac{P}{P_0} \right)^2 \quad (7)$$

The agreement of the model with the *ab initio* spectra of the water dimer is demonstrated in Fig. 5. The comparison is given for different pressures and temperatures.

3. Fitting the model to experimental data

The direct observation of the water dimer spectrum from water vapor at room temperature [7] demonstrated that, at least in the range up to 150 GHz, the peak positions correspond well to frequencies of the transitions $J \rightarrow J+1$, $K=0$, E_1 type, which can be calculated using the well known equation

$$\delta_j^{\text{exp}} = 2B(J+1) - 4D(J+1)^3 \quad (8)$$

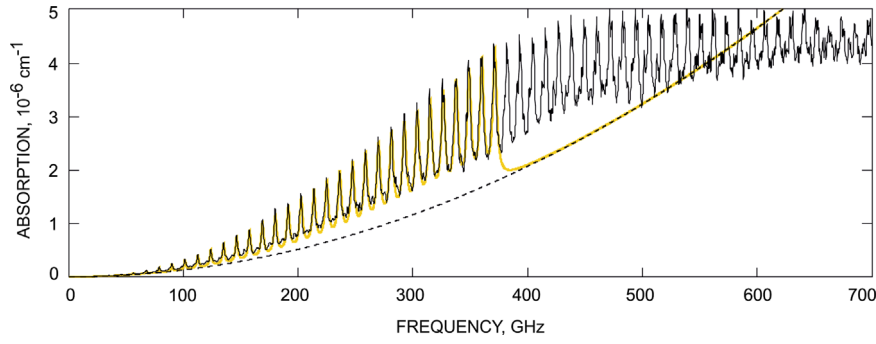


Fig. 4. Comparison of the calculated *E* spectrum of water dimer at 296 K and 13 Torr (thin black) with its modeling by function (Eq. (2)) including 33 Lorentzians (thick blue). The continuum-like part of the *E* spectrum is shown separately (dashed black).

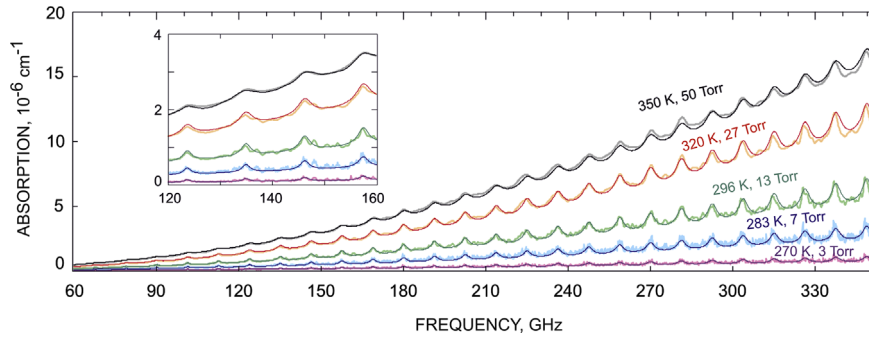


Fig. 5. Calculated millimeter-wave (A+B+E) spectra of water dimer at different temperatures and water vapor pressures (thick lines) and result of their modeling by Eq. (7) (thin lines). The inset displays a zoomed-in part of the same spectra in the 2-mm window of atmospheric transparency.

with effective rotational constant values $B=6.161611(21)$ GHz and $D=5.0079(91) \times 10^{-5}$ GHz as determined by Fraser et al. [16]. These frequencies should be used in the model instead of the ones obtained from Eq. (4).

Such a model can be used to describe how the spectrum of a bound dimer looks like under particular conditions. However, at least three adjustable parameters should be added to the model to be fitted to the experimental spectrum of water vapor recorded at given pressure (P_{exp}) and temperature (T_{exp}).

The first one is due to the uncertainty in the bound dimer equilibrium (or dimerization) constant (K_p), which determines the number of absorbing molecules and, therefore, the amplitude of the spectrum as given by Eq. (7). The model relies on the expression

$$K_p(T) = 4.7856 \times 10^{-4} \exp\left(\frac{1851.09}{T} - 5.10485 \times 10^{-3} T\right) \quad (9)$$

given in units of atm^{-1} , which has been fitted to *ab initio* calculations [13]. We added a multiplicative corrective constant (A_1), the meaning of which being a relative value of the dimerization constant.

The second parameter corresponds to the uncertainty in the widths of the dimer rotational peaks. Both values determining the peak width, namely, inhomogeneous and pressure broadenings are uncertain. However the model provides an approximate J – dependence of the width.

A second, adjustable, parameter (A_2) used for all peak widths given by Eq. (5) should resolve the problem.

The third parameter should take into account, as mentioned in the introduction section, the uncertain contribution of the bound dimers to the total bimolecular absorption and the role of the free molecular pairs and metastable dimers [11]. The contribution of far wings of the monomer lines should also be considered, although it is expected to be rather small in the studied frequency range [17]. Fortunately, all the previous experimental and theoretical studies demonstrated that in the millimeter wavelength range all these absorptions can be well approximated by quadratic monomial given by Eq. (1). Therefore, such a function with adjustable amplitude (A_3) should be added to the fitting model which can be finally written in the form

$$M(\nu) = A_1 \alpha(\nu, T_{\text{exp}}, P_{\text{exp}}, \delta_J^{\text{exp}}, \gamma_J + A_2) + A_3 \nu^2, \quad (10)$$

where α is the function defined in Eq. (7).

Fig. 6 shows that the model (Eq. (10)) is basically in good agreement with the experimental spectra recorded in the 110–150 [7] and 190–260 GHz [9] regions using the resonator spectrometer [8] at room temperature and almost the same pressure of water vapor. The contribution of water monomer lines subtracted from the spectra was calculated as a line-by-line sum of spectra due to the four major water isotopologues in natural abundances. All significant transitions with frequencies up to 1 THz reported in HITRAN [18] were included in the list using a Van Vleck–Weisskopf line shape. In the

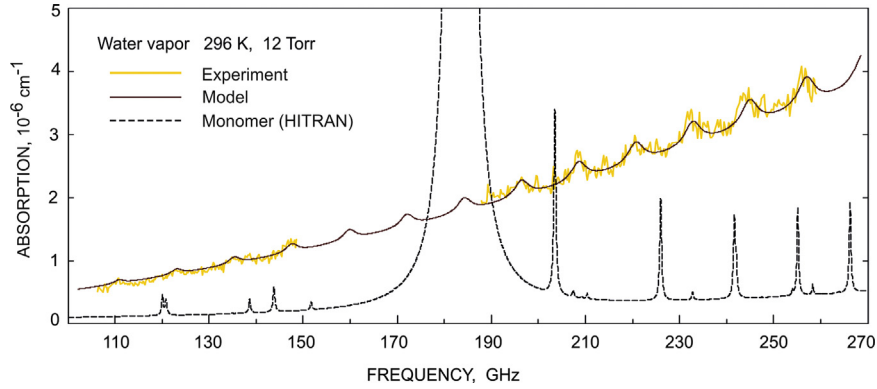


Fig. 6. Correspondence of the model (Eq. (10)) (smooth line) with the experimental spectrum of water vapor after the monomer contributions have been subtracted (broken lines). Bottom trace is the calculated water monomer spectrum. The model fitting parameter values are: $A_1=0.7$, $A_2=0.4$ GHz, $A_3=2.7 \times 10^{-7} \text{ cm}^{-1}/\text{GHz}^2$.

experimentally studied regions the monomer shows only a few weak, narrow, lines belonging to the partly deuterated water and to the excited bending state of H_2^{16}O (Fig. 6). Note that the monomer contribution to the total absorption is small.

Quantitative analysis of experimental recordings at different pressures and temperatures using this model may allow distinguishing the bound dimer contribution from the rest of absorption (analysis of which is of separate interest) and obtaining the dimerization constant value as well as the related dimer dissociation energy. Such an analysis of available experimental data [9] is beyond the scope of this paper and will be published elsewhere.

4. Atmospheric observation predictions

Our preliminary experiments with water vapor mixed with dry air demonstrated that the water dimerization constant in air is about the same as in pure water vapor [9]. This conclusion is very important for geophysical applications and it enables using the proposed model for assessing the possibility of direct detection of the water dimer in the atmosphere by means of available microwave radiometers. The atmospheric absorption variations related to the dimer peaks can be detected either by a ground-based or an airborne radiometer. The radiometer should have sufficient bandwidth for peak observation or should be able to simultaneously operate at frequencies corresponding to minima and maxima of the dimeric absorption.

A radiometer measures the power of the radiant flux in the direction of observation, which includes integrated thermal emission of the atmosphere in the proposed experiment. The radiant flux is usually measured in brightness temperature $T_b(\nu)$ that can be calculated using standard atmospheric pressure $P(h)$ and temperature $T(h)$ profiles characterizing the parameter value versus height from the Earth's surface (h), and the well known equation [19]:

$$T_b(\nu) = \int_0^H T(x) \alpha_{\text{total}}(\nu, P(x), T(x)) e^{-\int_0^x (\alpha_{\text{total}}(\nu, P(h), T(h)) / \cos(\theta)) dh} dx, \quad (11)$$

where α_{total} is the atmospheric absorption coefficient, θ is the Earth incidence angle and H is the height of observation of an

airborne device or the thickness of the atmosphere for a ground-based radiometer.

The total absorption can be expressed as the sum of components related to (i) atmospheric gases lines, (ii) water vapor self-continuum, (iii) water vapor foreign continuum, and (iv) dry atmospheric continuum. All these absorptions in the millimeter wavelength range have been relatively well studied. A general picture of the atmospheric brightness temperature spectrum can be calculated, for example, using the Millimeter-wave Propagation Model (MPM) [20]. Note that the model neglects minor atmospheric constituents. Such a spectrum corresponding to the zenith observation of the US standard summer atmosphere [21] (summer conditions are preferred for the dimer detection) is presented in Fig. 7. It is well known that the dominant contributors to the total absorption in atmospheric transparency windows are the self and foreign water vapor continua. Therefore, variations of the brightness temperature caused by the bound dimer absorption can be estimated from Eq. (11) taking the foreign continuum parameters from MPM and assuming that the self-continuum can be modeled by Eq. (7) with peak frequencies from Eq. (8) and parameters of the model fitted to the experiment (Fig. 6). Broadening of the dimer peaks caused by air pressure in GHz can be estimated as

$$\gamma_{\text{air}} = 0.004(P_{\text{total}} - P_{\text{water}}), \quad (12)$$

which should be added to the width of the Lorentzian profiles given by Eq. (5). A pressure broadening parameter value of 0.004 GHz/Torr in Eq. (12) approximately corresponds to the air broadening of the majority of lines of polar atmospheric molecules [18].

Results of such calculations corresponding to the 2- and 1.2-mm transparency windows, which are most promising for a direct detection of the dimer in the atmosphere from our point of view, are shown in the two insets of Fig. 7. The permanent part of the spectrum has been removed in both cases and only its variations are shown. The absolute value of the variations is about 1 K in the 1.2-mm window and 0.5 K in the 2-mm window. In both cases the variations are considerably larger than the sensitivity of modern radiometers in the considered bands at reasonable observation time.

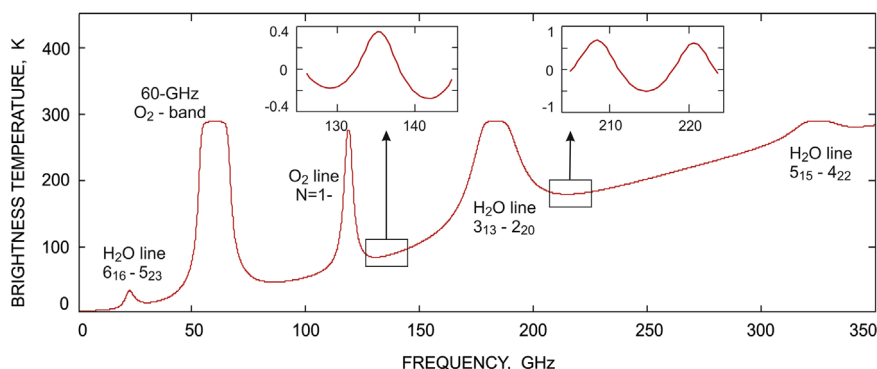


Fig. 7. Brightness temperature spectrum of the atmosphere in the millimeter-wave range calculated using the MPM model and US summer standard temperature and pressure profiles. The insets show alternation of the temperature in the 2- and 1.2-mm atmosphere transparency windows related to the water dimer absorption.

Consider as an example the sensitivity δT_b of the “Sequoia” receiver [22], which can be estimated using the well known formula

$$\delta T_b \sim \frac{T_n}{\sqrt{\Delta f \tau}}, \quad (13)$$

where $T_n = 60$ K and $\Delta f = 15 \times 10^9$ Hz are, respectively, the noise temperature and the frequency bandwidth of the receiver; τ is the signal acquisition time. At $\tau = 1$ s the receiver has a sensitivity of about 0.5 mK.

Zenith observation of the dimer-related atmospheric absorption is probably not optimal but it is the simplest way permitting us to show an order of magnitude of the expected signal and to demonstrate that it is possible to detect the brightness temperature variations.

Of course, observation of the water dimer spectral features is not limited to the particular frequency windows presented in Fig. 7. The corresponding variations of the brightness temperature may be calculated by analogy for any frequency band of existing or newly designed radiometers.

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