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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.

1. Introduction

The water dimer $(H_2O)_2$ 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 $Kp(T)$ [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:

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

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

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

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

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

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

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

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