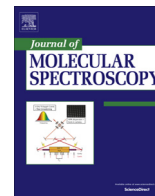




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# Spectroscopy underlying microwave remote sensing of atmospheric water vapor

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## ABSTRACT

The paper presents a spectroscopist's view on the problem of recovery of the atmosphere humidity profile using modern microwave radiometers. Fundamental equations, including the description of their limitations, related to modeling of atmospheric water vapor absorption are given. A review of all reported to date experimental studies aimed at obtaining corresponding numerical parameters is presented. Best estimates of these parameters related to the Voigt (Lorentz, Gross, Van Vleck – Weisskopf and other equivalent) profile based modeling of the 22- and 183-GHz water vapor diagnostic lines and to non-resonance absorption as well as corresponding uncertainties are made on the basis of their comparative analysis.

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## 0. Introduction

Water is one of the key molecules that determine the physical and chemical processes in Earth's atmosphere. Constituting less than 0.5% of the atmosphere's mass, water is responsible for about 70% of the radiation absorbed by the atmosphere, thus having a major impact on the radiation balance (see, for example [1,2]). Moreover, water vapor is a primary greenhouse gas in the Earth's atmosphere that produces a positive feedback, determining the weather and affecting global climate change [3].

Water molecules comprising the atmospheric water vapor absorb radiation in the whole wavelength range from radio to ultraviolet and beyond. This absorption is mainly due to the transition of molecules to higher vibrational and rotational energy levels corresponding to resonance spectral lines. These lines are rather intense, as the water molecule, being of low molecular weight, has a large permanent dipole moment. Since H<sub>2</sub>O is a light and very non-rigid asymmetric top molecule, its resonance lines are quite evenly distributed over the entire spectrum of electromagnetic waves. There are two mechanisms allowing the atmospheric water vapor to accumulate a considerable amount of energy and carry it with the air flow over long distances on a planetary scale. These are (a) the condensation of molecules with a possible subsequent transition into the solid phase, starting with

the collisional formation of double molecules, and (b) the energy distribution over internal degrees of freedom of the molecules. It is impossible to distinguish which of these two mechanisms plays the primary role. Qualitative estimations show that the distribution of roles between them may strongly depend on the weather conditions of a particular region. Due to its geometric structure, the water molecule has a relatively large (for the most common atmospheric molecules) number of the vibrational and rotational degrees of freedom – three vibrational and three rotational degrees of freedom. Internal energy accumulated by the atmospheric water vapor presumably has an influence on the formation and dynamics of tropical cyclones and is of importance not only for predicting rainfall amount, but also for early warning of possible extreme weather events. Precise, continuous quantitative information on the spatial distribution of atmospheric humidity is of prime priority for weather forecasting and monitoring of global climate change [4]. The most complete information of this kind on a global scale can be obtained from satellite remote sensing. The currently available network of specialized satellites provides global maps of the integrated thermal emission of the atmosphere at frequencies near the spectral lines corresponding to the lowest-frequency rotational transitions of water molecules (see, e.g. [5–7], and references therein). The characteristics of this radiation are unequivocally associated with the vertical profile of the absorption coefficient of water vapor, which is dependent on the concentration of water molecules, frequency, temperature, pressure, etc. However, a model of radiation propagation in the atmosphere is required to

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retrieve the quantitative information from satellite data. The rigor and accuracy of the model determines the accuracy of water vapor concentration retrieval. Any theoretical model requires knowledge of numerical coefficients, which are the model's parameters. Their values are usually found in experiment. It is obvious that most of the parameters are model-dependent. Improving the accuracy of their determination will increase the accuracy of modeling only in proportion to the “weight” of this parameter in the model, and only as long as the model can be considered adequate to the object or process being modeled. To be able to critically evaluate the modeling results, it is important to thoroughly understand the underlying principles of the model, its physical limitations, and the meaning of its numerical coefficients. Key aspects of molecular gas spectroscopy used for modeling of the atmospheric absorption are discussed in the first section of this paper. The second section analyzes the experimental data accumulated to date by the international research community, which provide the selected models with a set of numerical parameters required for quantitative modeling of the absorption. The third section presents a comparative analysis of these data. Finally, on the basis of this analysis, conclusions are made about the most promising frequency bands for satellite remote sensing of atmospheric water vapor.

## 1. Fundamentals of atmospheric absorption modeling

The fundamental law of variation of the power of radiation as it passes through a medium (in a particular case, through the atmosphere or its separate gas constituent) was formulated by Pierre Bouguer (1698–1758)

$$W(l) = W_0 \cdot \exp(-\alpha \cdot l), \quad (1)$$

where  $W$  is the transmitted radiation power passed through a matter,  $W_0$  is the incident power,  $l$  is the radiation path length, and  $\alpha$  is the absorption coefficient which is dependent on the radiation frequency and is actually the absorption spectrum of the matter. Note that it follows from classical Maxwell equations that the absorption coefficient is directly proportional to the imaginary part of the refractive index of the medium. The absorption coefficient and the real part of the refractive index are related to each other through the Kramers – Kronig relations. Depending on measurement method the retrieved value of the gas absorption coefficient can or cannot be affected by the refractive index. In the former case proper corrections should be carefully determined and taken into account.

The gas absorption spectrum is the sum of the resonant and non-resonant absorption. The resonant absorption is a property of individual, non-interacting molecules. It corresponds to the ideal gas, in which the collision of molecules with each other occurs instantly and fully elastically, and the gas is permanently in the state of thermodynamic equilibrium. The resonant absorption occurs at certain frequencies associated with the change in the angular velocity of the molecule (rotational transition) or the oscillation frequency (vibrational transition). The non-resonant absorption arises from the interaction of molecules with each other, i.e. due to the non-ideality of gas. Even during a collision that can be regarded as almost elastic from the classical point of view, the field of one molecule causes a redistribution of charges in the other, resulting in a small transient induced dipole moment. Non-elastic collisions lead to a short-term “adhesion” of molecules, and the formation of a new radiation-absorbing object. In both cases, a new additional absorption mechanism takes place, which acts for a very short time and, consequently, is characterized in the spectral region by smooth, compared to the resonance lines, frequency dependences, therefore leading to the non-resonance

absorption. Thus, the gas absorption coefficient can be expressed as the sum of the resonance lines and the non-resonance absorption resulting from non-elastic interactions of molecules

$$\alpha_{total} = \sum \alpha_{line} + \alpha_{non-resonance}. \quad (2)$$

### 1.1. Modeling of resonance lines of atmospheric water vapor

Water molecules in the Earth's atmosphere are almost entirely concentrated in the layer closest to the Earth's surface of about 10–15 km. Under these conditions, the shape of the resonance lines is completely determined by binary collisions, and the Doppler broadening can be neglected. The most popular shapes of the collision-broadened resonance line used to model absorption by atmospheric gases were comparatively analyzed in [8]. For this purpose, high-quality experimental data [9] on water vapor absorption near 22 GHz in air at atmospheric pressure were used. The analysis convincingly showed that the experimentally observed line best of all can be modeled by the van Vleck-Weisskopf profile [10]

$$\alpha_{line}(\nu, \nu_c) = \frac{S}{\pi} \left( \frac{\nu}{\nu_c} \right)^2 \left( \frac{\Delta\nu}{(\nu - \nu_c)^2 + \Delta\nu^2} + \frac{\Delta\nu}{(\nu + \nu_c)^2 + \Delta\nu^2} \right), \quad (3)$$

where  $\nu$  is the frequency of radiation, and  $\nu_c$ ,  $\Delta\nu$  and  $S$  are parameters of the line profile, which are the frequency of the center, the half-width at half amplitude and the integrated line intensity, respectively. A better, compared to other models, fit of the profile (3) to the observed resonance line shapes in wide-range experimental spectrum recordings of humid air at atmospheric or near-atmospheric pressures was also reported in [11,12].

The profile (3) was actually derived for ideal gas molecules, assuming that only two molecules are involved in each collision, and the collisions are considered instant and elastic. It was shown in [13] that the finite duration of the collision of molecules  $\tau_c$  in real gas means that the profile (3) is valid only when the frequency detuning satisfies  $|\nu - \nu_c| \ll (2\pi\tau_c)^{-1}$ . The smooth abruption of interaction of molecules with radiation during the collision leads to much faster decay of the line wing at detunings  $|\nu - \nu_c| > (2\pi\tau_c)^{-1}$  in comparison with function (3) (so called sub-Lorentzian behavior). However, real shape of line wings at large detunings is not known yet in spite of considerable theoretical efforts. The simplest way of modeling the resonance line absorption in this situation is just cutting the wings at  $(2\pi\tau_c)^{-1}$  assuming zero absorption at larger detunings (line wings cut-off). This procedure leads to unavoidable uncertainty in the non-resonance absorption determination, which will be discussed in Section 1.2. For the cut-off frequency it has been proposed [14] to use a value of  $25 \text{ cm}^{-1}$  (750 GHz). This corresponds to the time ( $\sim 2 \cdot 10^{-13} \text{ s}$ ) needed for a water molecule moving at an average relative thermal speed at room temperature to fly a distance of  $1.77 \text{ \AA}$ , which exceeds the maximum geometric size of the water molecule ( $\sim 1.2 \text{ \AA}$ ), but is less than the radius of the excluded gas-kinetic volume ( $\sim 2.5 \text{ \AA}$ ) and several times less than the spectroscopically determined radius of the collisional interaction cross-section between molecules. The choice of the maximum detuning is rather arbitrary, because its verification is currently impossible either by experimental methods or by first-principles calculations. The above evaluations show that the value of  $25 \text{ cm}^{-1}$  is rather close to the upper limit, but nonetheless is used in such well known propagation models as MPM [15] and MonoRTM [16].

All resonance line parameters defining the profile (3) are functions of temperature and pressure. The integrated intensity is directly proportional to the concentration of absorbing molecules, i.e. in the considered case – to the partial pressure of water vapor in the atmosphere. Its temperature dependence is given by the

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