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Millimeter wave continuum absorption in moist nitrogen at temperatures 261–328 K

M.A. Koshelev [1,*], E.A. Serov, V.V. Parshin, M.Yu. Tretyakov

Institute of Applied Physics of the Russian Academy of Sciences, 46 Ulyanov str., Nizhny Novgorod 603950, Russia

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ABSTRACT

The paper presents results of extensive experimental study of the water related continuum absorption in a mixture of water vapor and nitrogen in 107–143 GHz frequency range at accurately controlled laboratory conditions. Resonator spectrometer and modified method of measurement that minimizes systematic errors related to water adsorption were employed. It allowed investigation in temperature range 261–328 K, including a first-time laboratory study of the continuum at temperatures below freezing. Coefficients of the common empirical parameterization of the continuum including self (H_2O–H_2O) and foreign (H_2O–N_2) parts are derived and compared with results of the most known previous experimental and theoretical studies demonstrating very good qualitative and in some cases quantitative agreement. Dominating types of intermolecular interactions leading to the observed continuum are discussed.

1. Introduction

Millimeter wave remote sensing techniques play an important role for studying chemical and physical processes in the Earth's atmosphere as well as for understanding changes caused by anthropogenic activities. Modern instruments and methods of global monitoring of the Earth's atmosphere and underlying surface are sensitive to the accuracy of atmospheric absorption modeling and require accurate information on spectroscopic parameters used. The models describing attenuation of radiation by atmosphere take into account absorption due to resonance or local lines of atmospheric gases as well as non-resonance or continuum absorption. Growing abilities of modern remote sensing techniques put forth unprecedented requirements to the quality of spectroscopic parameters. For example, broadening parameters of the diagnostic atmospheric lines are expected to be known with an accuracy better than 3% [1,2]; spectroscopic accuracies of 0.2% or better are expected for the ACCURATE mission [3]. Though being relatively weak, the continuum absorption constitutes an essential fraction of the total absorption. In millimeter wave atmospheric windows of transparency its contribution can exceed the contribution of local lines by a factor of ten.

In spite of a long history of the continuum studies its nature is still a matter of discussions. Most consistent approach to the continuum understanding is summarized in the very recent work [4]. Critical review of other existent continuum interpretations is also given in [4]. Within the approach the continuum is considered as bimolecular absorption, which consists of three parts corresponding to different kinds of interacting molecular pairs, namely free monomers, metastable dimers and true bound dimers. Apparently all of the three parts hardly make distinguishable contributions, which are quantitatively different at different meteorological conditions and in different wavelength bands (see, discussions in [4,5] and references therein). To avoid the ambiguity the atmospheric continuum is usually described in applications by three-terms empirical expression (see, e.g. [6,7]), which is

* Corresponding author. Tel.: +7 831 4164866; fax: +7 831 4363792.
E-mail address: koma@appl.sci-nnov.ru (M.A. Koshelev).
[1] http://www.mwl.sci-nnov.ru

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fitted to the available experimental data. Two of these terms depend quadratically and linearly on water vapor partial pressure, and are called "self-" and "foreign water vapor continuum", respectively. The third term is related to pair collisions of foreign molecules (N_2–N_2, N_2–O_2, O_2–O_2, etc.). It is proportional to the square of the foreign gas partial pressure and is called "dry air continuum".

Experimentally the continuum absorption can be defined as the difference between measured total absorption and contribution from local lines. The latter is usually calculated as line-by-line sum using a uniform line-shape function with corresponding parameters of individual lines, which can be taken from a spectroscopic database (e.g., HITRAN [8]). It should be noted that the definition of the continuum is somewhat arbitrary: it strongly depends on the definition of the local lines absorption. Thus, refinement of spectroscopic parameters in the database may require new derivation of the continuum. Use of different line-shape functions could also significantly affect the continuum [6]. Therefore, any quantitative characterization of the continuum makes sense only for strictly defined contribution of the resonance absorption.

A number of laboratory experimental studies of water-related continuum absorption have been performed in millimeter/submillimeter region (see [6,9–17] and references therein) using either Fabry–Perot resonator or multipass cell technique. It was demonstrated in work [18] that results of all of these experiments could contain systematic uncertainty caused by water adsorption on mirrors, windows and coupling elements of the cavity (multipass cell or resonator) used in the spectrometers. Moreover, some systematic discrepancies in obtained results (e.g., in [14,15]) were potentially attributed to water adsorption by authors themselves. Briefly speaking, this effect arises from the principle of the absorption measurement. Spectrometer baseline (background or reference spectrum) is recorded when gas cavity is either empty or filled by dry non-absorbing gas; while for the continuum measurements a moist sample fills the cavity and water molecules can be adsorbed on surfaces of the mirrors, windows and coupling elements. Adsorbed water changes the "dry" baseline that appears as additional absorption in the moist sample. The continuum is the most sensitive part of total absorption in relation to this effect because of its smooth frequency dependence. The effect gets stronger with lowering temperature and increasing humidity of the sample.

To solve the problem, a new approach was proposed [17,18]. The approach is based on variation of the spectrometer optical path-length, which was for the first time implemented in resonator spectrometer in work [19]. Another modification of this method was realized in the new version of the spectrometer [18].

One more motivation of the present work is related to the fact that retrieval of the atmosphere parameters employs nowadays coefficients of the continuum obtained at temperatures, which are higher than usual sea level atmospheric temperature. Although not discussing the usual problems of experimental data extrapolation, we would like to stress that the continuum originating from various constituents of bimolecular absorption may have non uniform temperature dependence.

In the present work we applied the aforementioned method and technique [18] to accurate investigation of the continuum absorption in a mixture of water vapor with nitrogen at ten frequencies ranging from 107 to 143 GHz at atmospheric pressure and temperature varying from -12 to $+55$ °C. Additional analysis of the results was performed to demonstrate possible contribution of the systematic error due to water adsorption. Comparison of the obtained results with the experimental and theoretical data from most known previous studies was made and can be found in the discussion section of the paper.

2. Experimental details

The continuum absorption in the H_2O–N_2 mixture was investigated using modern version of the BWO based resonator spectrometer, which is described in detail in [18]. Briefly, the gas sample absorption measurement is based on precise determination of the Q-factor of the Fabry–Perot resonator employing fast digital phase-continuous recording of the resonance response and subsequent determination of its width. The spectrometer construction allows eliminating the systematic error caused by water adsorption on the resonator components. The module of two rigidly bounded resonators differing in length by exactly a factor of two is used. Special efforts are undertaken to get identical distribution of electrical field inside both resonators and most identical conditions for water adsorption on both resonator elements. Response widths are measured at the short resonator eigen-frequencies practically coinciding with the ones of the long resonator. The baseline (inherent resonator radiation loss) is measured separately for each resonator filled by dry nitrogen before each experiment.

The sample absorption was measured at ten frequencies: 107.68, 111.97, 115.39, 118.82, 123.11, 127.39, 130.39, 132.53, 137.25 and 143.25 GHz. The module of resonators was located inside the temperature controlled chamber allowing variations from -30 to $+60$ °C. In the present study the lower temperature limit was -12 °C since its further decrease led to extremely low water amounts in the sample and, consequently, to insufficiently large uncertainties of measured absorption. The sample relative humidity (rh) was varied from 0% to 60% at each temperature. The uniform conditions (temperature and humidity) of the sample inside the chamber (volume is about 180 l) were supplied by fan and controlled by a number of sensors. The temperature was measured within ± 0.5 °C accuracy by eight copper thermistors placed on each mirror and in space nearby each mirror. Two temperature/humidity sensors (Rotronic HygroFlex [http://www.rotronic-humidity.com/]) of ± 0.3 °C/± 1% rh accuracy were placed at the top and bottom of the vertically oriented resonator module. It is worth noting that during each experiment the largest vertical gradients inside the 0.9-meters height chamber did not exceed 1 °C and 1.5% rh for temperature and humidity, respectively. The chamber did not allow variations of the sample pressure so the experiments were carried out at atmospheric pressure. A calibrated pressure meter of 600–800 mmHg range used during the study