OBTAINING PRECISE CONSTANTS OF ATMOSPHERIC LINES IN THE MILLIMETER AND SUBMILLIMETER WAVELENGTH RANGES

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An important physical problem of supplying the Earth's atmosphere satellite monitoring with precise laboratory measurements of the line constants of atmospheric gases has been resolved. We developed a complex of spectrometers and techniques which improves the accuracy of line-constant measurements by about an order of magnitude. Systematic errors of measurements do not exceed the statistical ones. Agreement of the results obtained by two different spectrometers improves reliability of the measured constants. Examples of measurements of collisional constants (broadening, shift, and collisional coupling) for the most important diagnostic atmospheric lines of water and oxygen molecules are presented. A number of collisional constants of the molecules are obtained for the first time and some errors of the previous researchers are corrected. The measured parameters have been used for the international projects. Prospects for supplying planned satellite terahertz projects with precise laboratory data are pointed out.

1. Global monitoring of the Earth's atmosphere, data acquisition for weather forecast, and prediction of climate variations are fulfilled, in the long run, by microwave radiometric measurements from satellites. Measurement of altitude distributions of the atmospheric temperature and humidity is based on observation of spectral lines of atmospheric gases, primarily water and oxygen molecules. The interpretation of complex profiles of atmospheric lines observed from a satellite requires laboratory measurements of collisional-interaction constants of the corresponding molecule transitions, including broadening, shift, and collisional coupling (interference) of spectral lines. The accuracy of knowledge of the mentioned constants determines the accuracy of retrieved information.

Until very recent time, the required accuracy of laboratory measurements of these parameters has not been reached, especially in the millimeter and submillimeter wavelength ranges. For the most important diagnostic line of a water molecule at 183 GHz, the spread of values of the broadening constants measured in different laboratories reached 30%, and the shift constant was not measured in a laboratory at all [1]. The errors of determining the line broadening constants of an oxygen molecule reached up to 25% [2, 3]. In this case, if the error of assigning the broadening constant exceeds 5%, it becomes the main in the total error of determining the atmospheric parameters [4]. Improvement of the accuracy of laboratory studies of the atmospheric-line constants is a topical problem in experimental physics, which is of great applied value.

2. We developed a complex of spectrometers of the millimeter and submillimeter wavelength ranges with measurement and calibration techniques. As a result, the accuracy was increased by more than one order of magnitude amd the reliability of measurement of all mentioned molecule constants, such as broadening, shift, and collisional coupling of spectral lines, was improved.

The complex comprises two types of spectrometers which use backward-wave oscillators (BWOs): a spectrometer with radioacoustic detector (RAD) [2, 5] operated under pressures 0.1–10 Torr of the sample,

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and a cavity spectrometer [6] operated under the atmospheric pressure of the sample. A common feature of these devices is that the difficult-to-determine instrumental function, or the "base," against the background of which the lines are observed in conventional absorption spectrometers, is absent in the first order of smallness. In other words, in both spectrometers, the reception principle close to "zero" is realized and the main reason for the occurrence of a systematic error of measurement due to a significant, poorly reproducible background signal is therefore minimized.

Both devices are equipped with a precise digital system of the source frequency control, which was developed on the basis of phase lock by the harmonic of the computer-controlled synthesizer with a quantum frequency standard. For the cavity spectrometer, we developed a system of rapid frequency scanning in phase-lock mode with the continuity of the radiation phase preserved in switchings. Such a system ruled out the influence of the cavity eigenfrequency drift during measurement of the resonance-curve profile.

The remainder of the instrumental function in the RAD spectrometer is stipulated by absorption in the windows and the walls of a cell, and by interference in the microwave channel, which affects the losses introduced into the cavity, in the cavity spectrometer. In both devices, the remainder of the instrumental function is removed by a repeated record of a part of the spectrum with the replacement of the sample by a gas not absorbing in the microwave range and having similar molecular parameters (nitrogen). Precision control of the source frequency ensures good reproducibilty of records and an almost complete elimination of the instrumental function during the records subtraction.

3. The created complex of spectrometers and techniques is at present the best in the world for measurements of atmospheric-line characteristics. Examples of use of the complex are given in what follows.
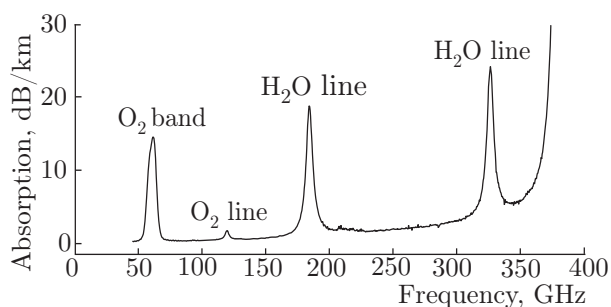

Fig. 1. A laboratory record of the atmospheric absorption spectrum in the 45–370-GHz range for a pressure of 730 Torr, a temperature of 296 K, and an absolute humidity of 5.3 g/m^3. The record shows an absorption band at 60 GHz, which consists of fine-structure lines of an oxygen molecule, a separate fine-structure line of oxygen at 118 GHz, absorption lines of water vapor at 183 and 325 GHz, and a wing of the absorption line at 380 GHz. Absorption line of water vapor at 321 GHz, whose intensity is about a factor of 40 less than that of the line at 325 GHz, coincides with the latter under the atmospheric pressure.

Figure 1 shows a survey record of the atmospheric absorption spectrum obtained at room temperature and atmospheric pressure using a cavity spectrometer in a frequency range of 45 to 370 GHz. A continuous record of the atmospheric absorption spectrum in this frequency range in a laboratory experiment was obtained for the first time with high accuracy and sensitivity. All the absorption lines presented in Fig. 1 are used for the atmosphere diagnostics. We obtained precise spectroscopic parameters for each of them using the above-described complex of spectrometers.

Figure 2 shows both the previous state of measurements and the results we obtained on the constant of line broadening by the air pressure for one of the most important diagnostic lines of water vapor 3_{13}–2_{20} at 183 GHz. It is seen that the measurement of the broadening constant of this water molecule line was admitted to be so important that a dozen of research groups have attacked this problem for over fourty years. Figure 2 also shows the difficulty with the solution of this problem. In the experiments performed by the previous groups of researchers, the error reached 30%, and the divergence of the results of different measurements exceeded severalfold the experimetal-error limits mentioned in their papers.

A significant (more than an order-of-magnitude) increase in accuracy in the course of our measurements [15, 16], which is seen in the plot, is combined with the fact that the results of measurements performed by two spectrometers with different principles of operation and working under gas-sample pressures differing by hundreds of times coincide within the limits of a statistical error. This ensures high reliability of the obtained values of the molecule constants. Precision measurements of the line broadening of an oxy-

Fig. 2. Results of measurements of the broadening constant γ of the water molecule line at 183 GHz by different research groups (presented in publication year order): point 1 corresponds to Rusk [7], point 2, to Dryagin et al. [8], point 3, to Frenkel and Woods [9], point 4, to Hemmi and Straiton [10], point 5, to Ryadov and Furashov [11], point 6, to Bauer et al. [12], point 7, to Bauer et al. [13], point 8, to Goyette and De Lucia [14], point 9, to Pumphrey and Buehler (MLS) [1], and point 10, to Pumphrey and Buehler (MAS) [1]. For obtaining points 11 and 12, we used the cavity spectrometer and the RAD spectrometer, respectively [15, 16]. The statistical error of measurement 12 amounts to only 0.007 MHz/Torr, which is less than the point size in the plot.
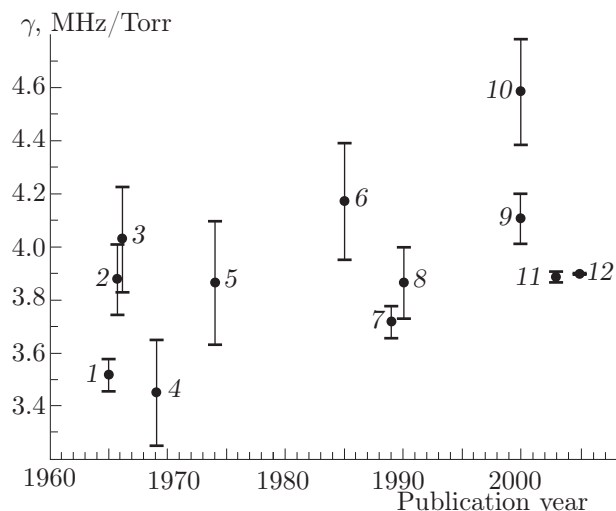
gen molecule were also performed using two spectrometers [2, 17–20]. The achieved accuracy 0.5%–2% of measurement of the line broadening constants exceeds at present the accuracy of knowledge of most of the molecule constants used for the satellite-data interpretation and can be considered satisfactory.

We also measured the constant of the pressure shift of the center frequency of the water line near 183 GHz [15, 16]. The shift measurement history of this line is much shorter. The air-pressure shift of this water line was discovered in 2000 during processing of the atmosphere limb sounding data by two tools, the MLS (Microwave Limb Sounder) mounted on the UARS (Upper Atmosphere Research Satellite) and the MAS (Millimeter-wave Atmospheric Sounder) mounted on the Space Shuttle [1]. Two values obtained by the authors of [1] differed twofold, but both indicated the existence of an effect coinciding in sign (and in order of magnitude). Allowance for the pressure shift of the water line significantly impaired the agreement of the calculated and experimental line profiles observed from the satellite. Estimating the case, the authors of [1] concluded that "Some parameters, including frequency shift by pressure, are difficult to measure in a laboratory. We think that the MLS tool can ensure a better measurement of the water-vapor line shift at a frequency of 183 GHz than any laboratory instruments known to us." Using the developed complex, the water line shift near 183 GHz was measured for the first time in 2003–2005. The measurement accuracy was 25% and 5% for the cavity spectrometer and the RAD spectrometer, respectively
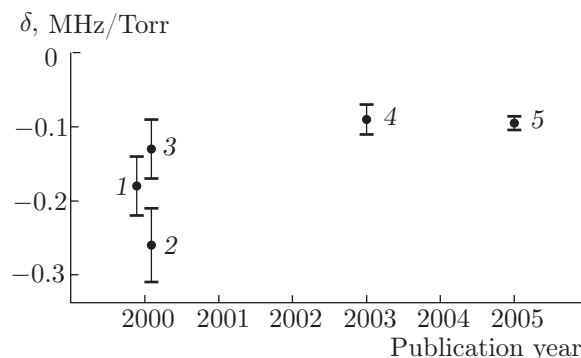

Fig. 3. Measurement results for the shift constant δ of the water molecule line near 183 GHz obtained by different research groups (presented in publication year order). Points 1 and 2 were obtained in [1] from measurements by the satellite-borne tools MLS and MAS, respectively, and point 3 obtained from the MAS data differs in the processing technique [1]. Points 1–3 are slightly separated on the horizontal axis for clarity. For obtaining points 4 and 5, we used the cavity spectrometer and the RAD spectrometer, respectively [15, 16].

[15, 16]. These results are presented in Fig. 3 together with the values obtained in [1]. It is well seen that the results of the previous measurements also show a large spread of data, and their diagreement is much greater than within the errors mentioned by the authors of [1]. The results that we obtained using different spectrometers for different sample pressures agree within the limits of statistical errors and have an order-of-magnitude higher accuracy. Thus, using the created complex, we also reached much more exact

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and reliable results in the measurements of a small (compared with the broadening) effect of the water-line shift by the atmospheric-gas pressure than the results obtained by the previous researchers. At present, we also measured for the first time the shift constants of the next-frequency atmospheric diagnostic water lines at 321, 325, and 380 GHz [21].

Precision measurements of the possible line shift by pressure were also performed in the studies of the oxygen spectra [2, 17–20]. Within the limits of the experiment accuracy, the shift of oxygen lines was not detected, but a qualitative upper bound of this effect, which was absent earlier, was established for the first time.

We measured for the first time the collisional-coupling coefficient for one of the most important diagnostic lines $N = 1-$ of an oxygen molecule at 118 GHz [20]. In the case of a single fine-structure line of an oxygen molecule at 118 GHz, the collisional coupling leads to the shape distortion and, as a consequence, shifts the center of the line observed in the atmosphere. The existence of such an effect was not noticed by the previous researchers, although a thorough analysis of Fig. 4 among the most extensive studies of this line [22] could help conclude, without making quantitative estimates, that the effect is present. The influence of the collisional coupling on the absorpion-band shape for fine-structure lines of oxygen at 60 GHz was detected and examined earlier in [23]. The collisional coupling effect in this case makes the absorption-band shape different from that obtained by simple summation of the absorption contours of all lines in the band. Measuring both the broadening of separate lines at a low pressure and the shape of the entire band at atmospheric pressure with accuracy higher than in [23], we not only determined more accurately the coupling coefficients of the first-order lines for an oxygen molecule, but also observed for the first time and quantitatively estimated the coupling effect for the second-order lines [18], while the theoretical calculations of this effect yielded only the form of the quantum-number dependence [24].

4. All the lines we studied are used for remote sounding of the atmosphere from spacecraft of NASA (National Aeronautics and Space Administration), ESA (European Space Agency), and NOAA (National Oceanic and Atmospheric Administration), such as EOS–MLS (Earth's Observing System–Microwave Limb Sounder), AMSU (Advanced Microwave Sounding Unit), SMR/Odin (Sub-Millimeter Radiometer onboard satellite "Odin"), as well as from high-altitude airplanes ER-2 and "Proteus," and on ground-based stations Barrow (USA) and other.

Using the developed spectrometers and research techniques, we solved an important problem of experimental physics, which is of great practical significance. The molecule constants we obtained to date have been employed in the European space program ESA MASTER (Millimeter-wave Acquisition for Stratosphere/Troposphere Exchange Research) [25] and international atmospheric databases [26]. The values of constants, which we obtained in the oxygen-spectrum studies, were used as reference for a study of the isotopic oxygen spectrum in the JPL (Jet Propulsion Laboratory) [27] and were applied in a new version of the common-use software MPM (Millimeter-wave Propagation Model), which was created in collaboration with the MIT (Massachusetts Institute of Technology) researchers [18]. Our precision measurements can also serve as a criterion for quality estimation of theoretical calculations of the collisional-interaction constants of different molecules.

5. The scope of satellite-based studies constantly increases, both in the number of observed molecules and in the spectral range, covering the submillimter and millimeter wavelength ranges for the planned vehicles (e.g., HIFI/Herschel (Heterodyne Instrument for Far Infrared obboard satellite "Herschel") of the European Space Agency, JEM/SMILES (Japan Experimental Module/Sub-Millimeter Limb Emission Sounder, an international space station) of the Japan Aerospace Exploration Agency, etc. Observation of spectral lines of the atmospheric minorities during limb sounding permits ecological monitoring of the atmosphere, studying the ozone-layer deterioration processes, etc. We have already increased the range of precision measurements using a RAD spectrometer up to frequencies exceeding 1 THz [19]. The range of a novel, high-precision cavity spectrometer was extended toward the submillimeter wavelength range [28]. The sensitivity and accuracy of the created complex will ensure laboratory measurements of the molecule constants required for space research.

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