

INVESTIGATION OF PURE WATER VAPOR ABSORPTION PROPERTIES IN THE LONG-WAVE SUBMILLIMETER TRANSMISSION WINDOWS

V.Yu. Katkov and N.I. Furashov

*Scientific - Research Radiophysics Institute , Nizhniy Novgorod
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The measurements of absorption of pure water vapor in dependence on pressure and temperature were carried out at the frequencies of 297, 343, 412, and 460 GHz corresponding to atmospheric transmission windows. In accordance with the theory of H₂O spectral line broadening the measured absorption is proportional to squared pressure with the value being essentially (up to 7 times) greater than that calculated with form factor according to kinetic equation. The temperature dependence of absorption is far stronger than calculated one and, in contrast to the latter, the former can be described by sum of two power functions with markedly different temperature exponents. The effects were discovered, which enable us to assume that real pure water vapor spectral line shape differs from Lorentzian one in the region of near line wings.

The experimental data on pure water vapor absorption in millimeter and submillimeter regions available from literature (see review in Ref. 1 and more recent Refs. 2–4) confirm the theoretical values⁵ of rotational line halfwidths and, at the same time, show that in transmission windows the measured absorption is far stronger than the theoretical one (up to 10 times, Ref. 6) in comparison with that observed in atmospheric water vapor (up to 2 times, Ref. 7). The latter circumstance emphasizes that the study of pure water vapor absorption spectrum is important for practical applications because far from the line center the pure water vapor absorption coefficient, theoretically, should be equal to the component of atmospheric absorption coefficient, which is quadratically dependent on air humidity. There are only a few data on this component available now^{8–11} and the existing information on pure water vapor absorption, which could be used to study the temperature and humidity dependences of atmospheric absorption in the transmission windows, is rather contradictory as concerning both the value of absorption (cf. Ref. 12 with Ref. 13, Ref. 14 with Ref. 15, Refs. 15–16 with Ref. 17) and its temperature dependence (cf. Refs. 6 and 18 with Refs. 13, 17, and 19). Moreover, one can see from comparison of the results from Refs. 15–17 with those from Ref. 9, Ref. 6 with those from Ref. 10, and Ref. 17 with those from Ref. 11 that even the possibility of making such a correlation needs for a serious experimental examination. To obtain the data that could clarify and correct the existing ideas on water vapor absorption properties, the measurements of pure water vapor absorption coefficients depending on temperature and pressure were carried out at 297, 343, 412, and 460 GHz frequencies lying in the windows of relatively high transmission of the atmosphere.

MEASUREMENT TECHNIQUE

The measurements were carried out using the inverse wave tube (IWT) radiospectrometer with a multipass vacuum cell.²⁰ The radiation beam incident onto the cell underwent 57 reflections from mirrors and came back to the input window covering the path of 140 m length. The drift of the detector sensitivity and instability of losses in

quasioptical channels out of the cell can cause errors in measurement of absorption. To exclude this error a plate of Getinaks with suitable reflection coefficient was placed in front of the input window. The values of transmission of both evacuated and water vapor filled cell were obtained relative to the value of signal reflected from the plate. The optical thickness of the plate was not less than 25. During the experiments the evacuated cell was cooled by air blowing (in cold seasons) or heated with an electric heater. The temperature in the cell was monitored at seven points. The maximum difference in the thermometers readings due to inhomogeneity of temperature was ± 1 K near 255 K, ± 0.5 K near 300 K, and ± 3 K near 350 K. When the temperature reached a required value, the relative value of transmission was recorded. Then the water vapor was injected by portions into the cell from the retort with degaussed distilled water. About 20 minutes later after each injection, the transmission was repeatedly recorded. The pressure was measured with an oil manometer, the error of measurements being about 0.1 Torr.

So the measurement process consisted of the following stages. First, the water vapor was injected into the evacuated cell, second, water vapor was kept in the cell during a long time, and, third, quickly (in a minute) the cell was evacuated. This procedure showed that no hysteresis effects in the pressure behavior of absorption were observed. As a consequence, the influence of moisture adsorbed by reflecting plates of cell mirrors can be neglected. The calculation of reflection coefficient of a mirror coated with water film showed that the absorption measurement error due to adsorption can exceed the sensitivity of a radiospectrometer (~ 0.1 dB/km) only when the film is thicker than $2 \mu\text{m}$. Since according to experimental data^{11,21} the water film thickness on a smooth metal plate at the relative humidity less than 90% is, as a rule, far smaller than $0.2 \mu\text{m}$, the presented results can be considered free from this type of errors.

MEASUREMENT RESULTS AND DISCUSSION

The absorption measured at $\nu = 297, 343, 412,$ and 460 GHz frequencies at the temperature T from 285 to

348 K and pressure e from 0 to 30 Torr at relative humidity up to 90% proved to be proportional to the squared pressure everywhere, what well agrees with the H₂O spectral line broadening theory. However, the values of absorption are 1.3 to 7 times (depending on ν and T) stronger than that calculated (analogous to Refs. 9 and 11) using form factor according to kinetic equation⁷ and line halfwidths from Ref. 5.

Figure 1 presents the results, which demonstrate linear dependence of the absorption coefficient Γ on squared pressure at $T \approx 297$ K. Because these results were obtained at radiospectrometer regime with a fixed frequency, Fig. 1 presents the four independent runs. The root-mean-square spread of experimental points relative to approximating straight lines is in this case 0.1–0.15 dB/km. At other temperatures similar results were mainly obtained in the regime of frequency scanning, i.e. the absorption at four frequencies was measured in turn after each water vapor injection. In the latter regime the measurement accuracy is 2 to 3 times poorer what may be explained by insufficient reproducibility of amplitude-phase distribution of the emission source field at repeated setting of the frequency.

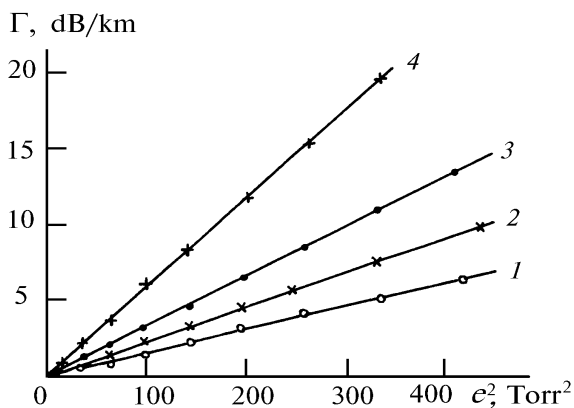


FIG. 1 Pure water vapor absorption coefficient as a function of squared pressure at temperature $T \approx 297$ K: 297 (1), 343 (2), 412 (3), and 460 GHz (4).

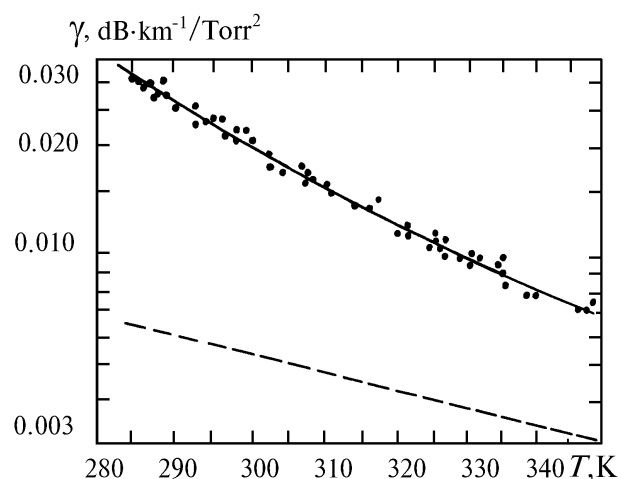


FIG. 2 Temperature dependence of pure water vapor absorption at 343 GHz. Points are the results of measurements, solid line is the approximating curve, dashed line is the theoretically calculated data.

The experimentally obtained temperature dependence of absorption at all four frequencies proved to be far stronger than the calculated one. Moreover, in contrast to the calculated one, it can not be approximated by a power function good enough. For example, Fig. 2 presents the experimental and theoretical temperature dependences of the normalized absorption coefficient γ ($\gamma = \Gamma/e^2$) at 343 GHz frequency. The γ values are given in a logarithmic scale, in which the power function is plotted as a straight line. The solid line in Fig. 2 approximating the experimental points is rather different from the straight line and agrees with the dependence of the following form:

$$\gamma(T) = \gamma_1^0 \left(\frac{300}{T}\right)^{n_1} + \gamma_2^0 \left(\frac{300}{T}\right)^{n_2} \quad (1)$$

Since in the temperature region investigated the observed nonlinearity is not strong enough to enable determination of all four parameters of Eq. (1) independently, the processing of data was carried out assuming that n_1 exponent is of theoretical value. When making this assumption we first aimed at describing the portion of the total absorption which is caused by the absorption lines of H₂O at close frequencies of 325, 380, 448, and 557 GHz that contribute from 65 to 85% to absorption at all frequencies under study. Moreover, we took into account the experimental result from Ref. 22, which allows us to believe that the temperature dependence in the near wings of lines ($|\nu - \nu_0| \leq 100$ GHz) is close to the theoretical one.

The values of γ_1 , γ_2 , and n_2 parameters of approximation (1) obtained by the least square method (with uncertainties $\sim 30\%$) are presented in Table I together with the theoretical values of γ_1 and n_1 . The rms deviations of measured $\gamma(T)$ values from the approximating curves (1) with the parameters from Table I are equal to 6, 4, 5, and 3% at frequencies of 297, 343, 412, and 460 GHz, respectively.

TABLE I. The theoretical and experimental values of the approximation (1) parameters.

Parameters	ν , GHz				Notes
	297	343	412	460	
γ_1^0	0.0025	0.0054	0.0108	0.0305	Theory
n_1	3.7	3.5	3.6	3.3	
γ_1^0	0.0065	0.008	0.016	0.031	Experiment
γ_2^0	0.0065	0.012	0.014	0.022	($n_1 = n_1^{\text{theor.}}$)
n_2	14	11	12	10	

Note: The values of γ are given in dB km⁻¹/Torr².

Thus, the experimental $\gamma(T)$ dependence can be approximated by a sum of two components with essentially different temperature exponents ($n_1 \approx 3.5$, $n_2 = 12 \pm 3$), what is indicative of the presence of two different absorption mechanisms. The second absorption mechanism could be solely due to H₂O rotational band broadened by pressure or due to the additional absorption bands stimulated by molecular collisions^{23,24} or due to absorption bands belonging to (H₂O)₂ dimmers^{17,25–27}.

Now it is not clear yet, because modern spectral line broadening theories²⁷⁻³⁰ admit the existence of strong temperature effect on the shape of far wings of absorption lines.

It should be noted that pure water vapor absorption coefficient measured at 343 and 412 GHz frequencies at $T = 306$ K is 50% greater than that predicted by a quadratic on air humidity components of the atmospheric absorption coefficients,⁹ for the same frequencies and temperatures. In other paper we are going to show that the most probable reason of such a difference is a decrease in γ_1 coefficient occurring when dry air is added to pure water vapor. This effect and tendency of γ_1 value to be in excess of the calculated one revealed in these measurements (see Table I) appear to be consequences of a marked deviation of a pure water vapor spectral line shape from the Lorentzian one in the region of near line wings. The results of our preliminary measurements of spectral distribution of absorption in the wings of absorption line at $\nu_0 = 380$ GHz ($\nu = 354-400$ GHz, $e = 20$ Torr, $T = 303$ K) also confirm this assumption. Small ($\sim 10\%$) frequency dependent deviations of the measured absorption from that expected from theoretical calculations and experimental data obtained at $\nu = 297, 343, 412,$ and 460 GHz were revealed, which cannot be

explained only by uncertainties in the parameters of this line. The deviations are rather large with respect to absorption at the line at $\nu_0 = 380$ GHz because, if tuning out of the resonance frequency by more than 10 GHz, the calculated contribution of this line to measured absorption becomes smaller than 50%, and at 354 and 400 GHz it is only 14 and 20%.

COMPARISON OF THE RESULTS WITH THE DATA AVAILABLE FROM LITERATURE

The absorption by pure water vapor in the transmission windows from the frequency range studied was measured by two research groups (see Refs. 15-16 and Ref. 17). The comparison of results of our measurements and that of Refs. 15-17 are presented in Table II. Data from Refs. 15-17 were obtained at ν and T values slightly different from that presented in Table II, so we corrected these data using obtained frequency and temperature dependences of the excess (with respect to calculated one) absorption. The corrections added are smaller than the errors of measurement in Refs. 15-17. It can be seen from Table II that our results confirm those from Ref. 17, just making them more precise, and essentially correct the data from Refs. 15-16, which seems to be 1.5 times overestimated.

TABLE II. The comparison of our results (o.r.) with the experimental data from Refs. 15-17 ($T = 296$ K).

	ν , GHz				
	297	343	412	460	Notes
γ , dB·km ⁻¹ /Torr ²	0.023±0.009	0.034±0.008	0.051±0.013	—	Refs. 15 and 16
	—	0.021±0.008	0.037±0.005	0.065±0.004	Ref. 17
	0.015±0.001	0.022±0.001	0.033±0.002	0.058±0.002	o.r.

Joint analysis of our results and those from Refs. 6, and 12-14 ($\nu = 138-245$ GHz) made in terms of the excess absorption allow us to conclude that the value of absorption measured in Ref. 14 at the frequency of 245 GHz is 2 to 3 times overestimated and that measured in Ref. 13 at 190 GHz frequency seems to be 20 to 40% overestimated one too.

The above mentioned Ref. 17 contains the information about temperature dependence of the excess absorption in 360-950 GHz range, however, near 400 GHz it is very uncertain. The most reliable data from Ref. 17 corresponding to 600-950 GHz frequency range do not contradict our data. It is possible to say that our data on temperature dependence well agree with those obtained from investigation of atmospheric and pure water vapor¹⁰⁻¹³ (138 and 190 GHz) if analyzed in terms of the excess absorption. As a consequence, the result from Ref. 18, according to which the excess absorption of pure water vapor at 115-126 and 213 GHz frequencies is approximately proportional to T^{-38} at $T = 280-300$ K, seems to be very doubtful.

CONCLUSION

The results of investigation of pure water vapor absorption properties presented make the available experimental data essentially more correct and complete. The main result of investigation is in the following. The strong inverse temperature dependence of the absorption in the millimeter and long-wave submillimeter transmission windows, the first report on which appeared

in the late sixties,¹⁹ in our opinion, must be now considered as a reliable scientific fact.

More fine effects we have revealed in our study based on the assumption that actual profile of pure water vapor spectral lines differs from the Lorentzian profile in the region of near line wings are not so reliable and require a more comprehensive study. As we think, the important information for solution to the problem on the line shape could be obtained from measurements of the spectral structure of absorption near $\nu_0 = 557$ GHz H₂O line. This very strong line contributes not less than 50% into the total absorption by pure water vapor in a relatively wide spectral range $|\nu - \nu_0| \leq 60$ GHz, what provides quite favorable conditions for investigation of its wings in the region of shifted frequencies, say a tens to hundreds halfwidths.

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EDITOR'S NOTE

Though the problem on propagation of submillimeter waves is a little bit out of the topical range of the Journal (its appearance in the journals *Izv. Vysh. Uchebn. Zaved.*, *Radiofiz.* or *Radiotekhn. Electron.* would be more natural) we have decided after certain discussions to publish it, since it presents some new experimental material interesting and important for the general problem on the spectral line shape, including the optical spectral range.

Professor S.D. Tvorogov