ON THE SPECTRAL LINE SHAPE IN DIFFERENT H_2O BANDS IN THE NEAR INFRARED SPECTRAL REGION

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Absorption coefficient of H_2O *broadened by* N_2 *in the spectral range* 9450–9475 cm^{-1} *is calculated using line-by-line method with different empirical and theoretical expressions for the spectral line shape. The comparison made between the calculated data and those obtained in laboratory and field measurements shows that a good agreement between the calculated and laboratory measurement data on the absorption coefficient can be achieved by changing the line contour. However, to explain measurement results obtained in a dry cloudless atmosphere one should take into account some additional factors different from the molecular absorption.*

1. Modern spectroscopic data banks involve tens of H_2O absorption bands in the near infrared region. The absorption in this spectral region is of great importance for climate studies, including such as the calculation of solar heating of the atmosphere or the estimation of the excess absorption in the clouds (Refs. 1 and 2). The question on the nature of excess absorption of short-wave radiation in clouds is still being discussed in the literature, and the absorption by water vapor is one of the versions of this effect origin. Moreover, the data of recent field measurements (Refs. 4 and 5), in addition to those from Ref. 3, evidence that the atmosphere exhibits the extinction property for the short-wave radiation that depends on the moisture content in cloudless atmosphere either. Since the measured absorption coefficient is proportional to the absolute air humidity, it cannot be caused by light absorption by the coarse aerosol fraction. Thus the possibility of describing the properties of the above mentioned absorption, may apparently lie in the assumption of either the absorption by submicron aerosol or by water vapor because of some its peculiar spectroscopic features. The excess absorption discussed, being, as a rule, measured in the intervals between the water vapor absorption bands, has approximately same value in a wide spectral range from 0.44 to 3.97 μm. For this reason it is quite natural to call it "the atmospheric continuum".

This continuum, being caused by the molecular absorption (in the case discussed this is the absorption in the line wings) can be called as a "spectroscopic" continuum. The attempts to estimate the spectroscopic continuum have been undertaken in Refs. 5 and 6, where the water vapor absorption coefficient in the case of line broadening by nitrogen is calculated using the Lorentz line shape cut at a distance of 500 cm^{-1} from the line center. Since the deviations of the line shape towards the exponential fall off have been noticed to occur, in the case of the H_2O–N_2 gas mixture, at smaller than 500 cm^{-1} frequency shifts, the calculated values of the absorption coefficient could be taken as its upper limit, while, however, this value is being found to be significantly lower than the measured values. From this the conclusion has been drawn that the measured absorption has nothing to do with the molecular absorption. The change of the line shape has certainly result in different calculated values of the absorption. In this paper we consider the influence that the change of line shape may show on the calculated value of the absorption coefficient.

2. The line shape, in the central part of a line, and, correspondingly, the behavior of the atmospheric transmission function within the absorption bands are studied quite well. However, since we discuss here the use of spectroscopic data in climatic models, the estimation of atmospheric extinction for radiation in the most transparent spectral regions are of our primary concern. The extinction of radiation in these regions is, as a rule, due to absorption in the wings of spectral lines. It is known that the line shape in the wing of a spectral line differs from the Lorentzian one, and can exceed it in the near wing thus resulting in the exponential fall off of the absorption in the far wing. Despite a close attention the researchers pay to the theoretical description of the line shape its behavior in the wing is still debated.

The absorption of light by water vapor is the main cause of the atmospheric extinction for radiation within the transmission windows. There are no doubts in the existence of continuous absorption in the atmosphere related to the atmospheric moisture both in the known region 8–12 μm and in the transmission windows at shorter wavelengths. Though being a commonly accepted conception for the range of 8–12 μm the thesis on the radiation extinction due to absorption in the absorption line wings can not be

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considered as a doubtless one regarding other transmission windows.

When describing the absorption of light in the atmospheric transmission windows some empirical relationships are used for the absorption coefficient, as well as empirical line shapes and the line shapes obtained theoretically.

There are empirical relationships for the absorption coefficient in the range 8–12 (Ref. 7–10), 3–5 (Ref. 10) and 0.7–3.85 μm (Ref. 1). The empirical relation for the water vapor absorption line shapes are given in the papers by Thomas and Nordstrom (Ref. 11) and Clough (Refs. 12 and 13). When deriving the empirical relations for the line shapes certain theoretic conceptions are, as a rule, used. However, already at the early stage of estimations parameters are being introduced into consideration that can hardly be explained from the physical point of view, and the choice of which is only done to provide for coincidence between the calculated and measured values of the absorption coefficient.

The theoretical line shapes result from a rigorous reasoning, but certain approximations are quite natural. Thus introduced parameters have quite an obvious physical meaning, and these values can be, if only in principle, estimated.

Such a line shape has first been derived, based on the theory of line wings in 1976 (Ref. 14) (see also Ref. 15) for the lines of the water vapor rotational band to explain the light absorption in the gas mixture of H_2O–N_2 in the range of 8–12 μm. Somewhat different analytical approach has been proposed in Ref. 16 for the ranges of 8–12 and 3–5 μm.

In the papers, also devoted to analytical relations for the water vapor absorption line shape, Ma and Tipping (Refs. 17 and 18) have significantly improved the calculation technique of the quasistatistical theory of line shape, first proposed and tested by Rozenkranz (Ref. 19).

3. As a rule, all the above mentioned papers use, as a test, the experimental data obtained by Burch (Ref. 20) in the regions of 8–12 and 3–5 μm. There are only individual measurements for the visible and near IR-ranges. Thus in Ref. 21 one may find the value of the absorption coefficient at the frequency $\nu = 9466\ \text{cm}^{-1}$ (in the transmission window at 1 μm) to be equal to $6 \cdot 10^{-10}\ \text{cm}^{-1}$, obtained with the use of an interferometric calorimeter at the water vapor partial pressure $P_{H_2O} = 16.5$ Torr, the pressure of nitrogen, as a broadening gas, $P_{N_2} = 1$ atm, and at temperature of 30°C. The measurements of the absorption by air at the water vapor partial pressure from 5 to 15 Torr at different wavelengths in the range 0.5–1.35 μm have been carried out in Ref. 22 using the methods of laser spectrophotometry and laser optoacoustic spectroscopy. In all series of the measurements no any dependence of the absorption on the moisture content has been recorded because the threshold sensitivity of the instrumentation used does not allow one to measure the values $k \le 10^{-7}\ \text{cm}^{-1}$. For that reason it can be accepted that the water vapor absorption coefficient in the spectral region considered does not exceed $10^{-7}\ \text{cm}^{-1}$. No other laboratory measurements of the absorption coefficient in the visual and near infrared regions are known for us.

4. The calculations of water vapor absorption coefficient in the near IR-range made by Ma and Tipping (Refs. 17 and 18) for the cases of self-broadening and broadening by nitrogen gave much smaller absorption coefficients than those observed in field measurements, and approximately two times lower than those measured in laboratory conditions (Ref. 21).

We should like to underline here that in the calculations of the absorption in the visible and near IR regions, when using both theoretical and empirical line shapes, the relations are most often used for the line shape obtained for the range 8–12 μm.

In general, the spectral line shape changes from band to band and depends on the type of the broadening gas. This fact is out of doubt when we speak about the CO_2 spectra in the IR range. Thus, the difference in the deviation from the Lorentz line shape in the bands 4.3, 2.7 and 1.4 μm of the CO_2 at self-broadening and in the cases with N_2, Ar and He as the broadening gases has experimentally been recorded in Ref. 23. An interpretation of this result on the basis of the theory of line wings has been given in Refs. 14 and 15. The change of the line shape that should occur when coming from band to band has just begun to be realized as a natural circumstance for the water vapor absorption coefficient. We know the only paper where different line shapes are used when treating different water vapor absorption bands is the paper by Thomas and Nordstrom (Ref. 6), who obtained their empiric line shapes for the rotational, ν_2 and ν_1 and ν_3 bands. Their results evidence that, in general, the deviations from the Lorentz line shape can grow with the decreasing wavelength, as seen from Fig. 1.

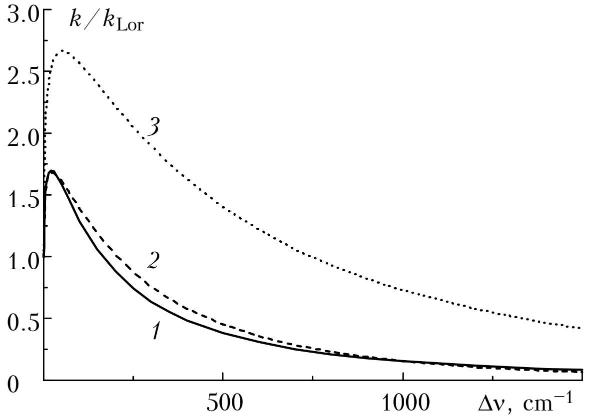

FIG. 1. Deviations from the Lorentz line shape for the Thomas-Nordstrom empirical line shapes $P_{H_2O} = 0.02$ atm, $P_{H_2O+N_2} = 1$ atm; $\nu_0 = 199.935\ \text{cm}^{-1}$ *(1)*, $\nu_0 = 1600.849\ \text{cm}^{-1}$ *(2)*, $\nu_0 = 3499.883\ \text{cm}^{-1}$ *(3)*.

5. In the present paper the water vapor absorption coefficient is calculated for the region near the frequency of 9466 cm^{-1}, for which there are data of laboratory measurements available. In these calculations we use a number of empirical and theoretical line shapes. The aim of these calculations was to answer the question on whether or not can the line shape variation, within reasonable limits, result in other conclusion than the conclusion on the impossibility of describing the data of field measurements (Ref. 3 and 5) based on the molecular absorption.

It is known that the behavior of the absorption coefficient within the boundaries of the absorption bands, that is in a close vicinity of the line centers, under standard conditions is described by the Lorentz line shape. One of the approximation methods for calculating of transmission is the line-by-line method with the Lorentz line shape cut at a certain distance from the line center.

It is clear that the criterion to be used for determining the boundaries of the Lorentz line shape should be the agreement between the calculated absorption coefficients or transmission functions and the experimental ones. In this way, the difference between the actual and the Lorentz line shape is approximately taken to account. Note that widening of this interval may result in almost arbitrary increase in the absorption coefficient value in this interval (see Fig. 2). However, there is no physical sense in such a big difference between the actual and Lorentz line shape that may result from modeling by extending the Lorentz contour to a large distance.

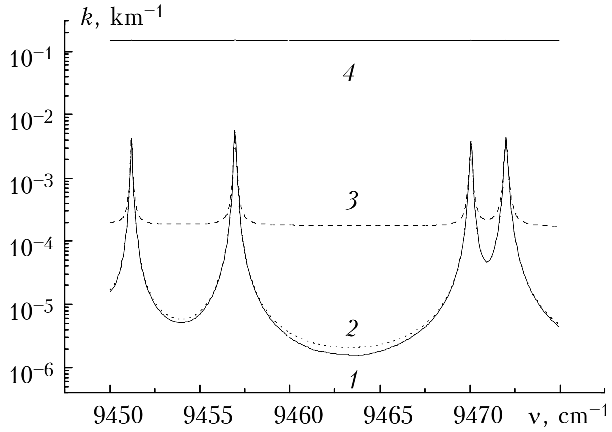

FIG. 2. Absorption coefficient of the gas mixture H_2O–N_2 *for several values of the Lorentz line shape widths at* $T = 296$ K $\rho_{H_2O} = 16.5$ g/m^3: $\Delta\nu = 20$ cm^{-1} *(1),* $\Delta\nu = 100$ cm^{-1} *(2),* $\Delta\nu = 1000$ cm^{-1} *(3), and* $\Delta\nu = 10000$ cm^{-1} *(4).*

Of course, no universal Lorentz boundaries for every spectral region and broadening gases can be found, and such a method for the description can have only a limited application, as by the way, any other empirical method.

The calculated results on the H_2O absorption coefficient at broadening by N_2 at $T = 296$ K, $P_{H_2O} = 0.02$ atm, $P_{H_2O+N_2} = 1$ atm obtained using different empirical and theoretical line shapes are shown in Fig. 3. The absorption coefficients, that result from the Lorentz line shape extending to 20 and 1000 cm^{-1}, as well as from the Thomas-Nordstorm contour obtained for three water vapor absorption bands and the line shape by Clough are presented in this figure. The line shape obtained based on the theory of line wings (Refs. 14 and 15) for describing the nitrogen-broadened water vapor absorption lines in the transmission window 8–12 μm leads to a good agreement with the experimental data in this spectral region (Fig. 4).

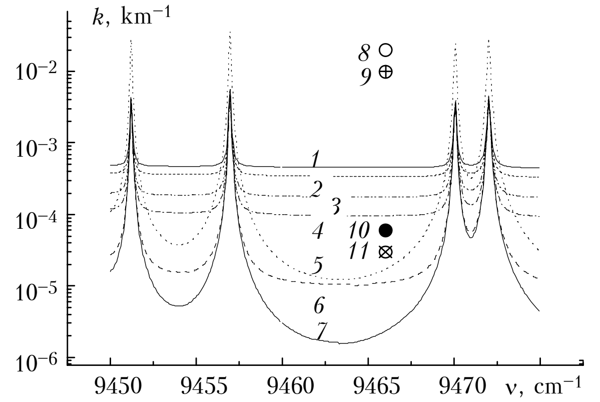

FIG. 3. Absorption coefficients of the H_2O–N_2 *gas mixture in the vicinity of* 9466 cm^{-1} *frequency calculated using different line shapes: Thomas-Nordstorm line shape chosen for the rotational* H_2O *band (1), Thomas-Nordstorm line shape for the* ν_1, and ν_3 *bands of* H_2O *(2), Lorentz contour cut at the distance of* 1000 cm^{-1} *from the line center (3), Thomas-Nordstorm line shape for the* ν_2 H_2O *absorption band (4), the Clough line shape (5) the line shape that follows from the theory of the line wings, (6), (7) the Lorentz line shape cut at the distance of* 20 cm^{-1} *from the line center, (11) the calculations by Ma and Tipping (Ref. 18). The experimental data: (8) field measurements (Refs. 4 and 5), (9) measurement data from (Ref. 22), (10) laboratory measurements (Ref. 21).*

It has also been used in calculations of the absorption coefficient in the H_2O–N_2 mixture in the spectral region considered. The absorption coefficient value obtained using this contour at the frequency 9466 cm^{-1} is close to the value estimated by Ma and Tipping for the sum of the absorption coefficients caused by self-broadening and broadening by nitrogen. The line shape chosen has been used for all the lines in the spectral interval studied when calculating every curve presented.

It is seen from Fig. 3 that the absorption measured in Ref. 21 can be interpreted with the use of the molecular absorption, but for the most reliable conclusions it is preferable to have more measurement data in the near IR transmission window. The absorption obtained from the field measurements (Refs. 3–5) can hardly be described only by changing the absorption line shape. All values of the absorption coefficient calculated are obviously lower than those obtained from field measurements.

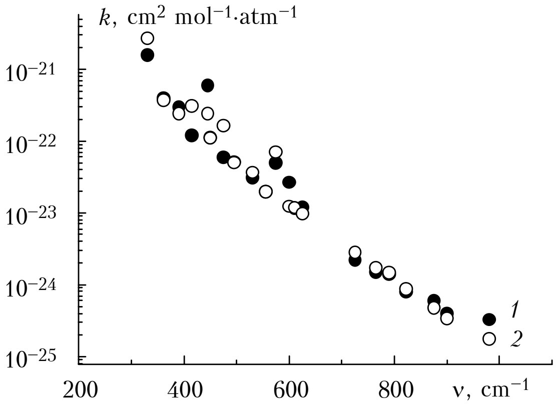

FIG. 4. The values of the absorption coefficient in the gas mixture $H_2O–N_2$ *at* $T = 296$ K; *experimental (Ref. 20) (1) and calculated in accordance with the theory of line wings (Refs. 14 and 15) (2).*

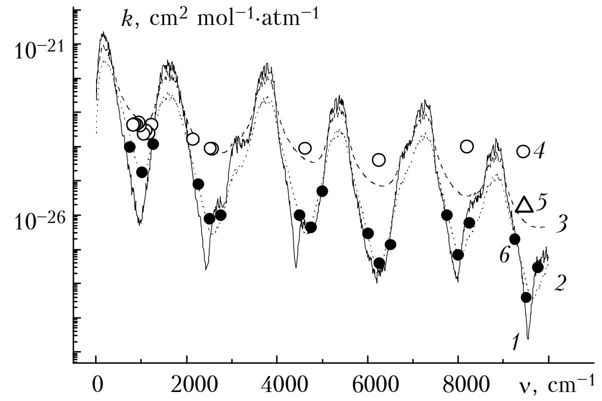

FIG. 5. The values of the absorption coefficient of the gas mixture $H_2O–N_2$ *in the IR region excluding the contributions from lines in the range* ± 25 cm^{-1} *about the current frequency: (1) calculation using Clough continuum (Ref. 12), (2) calculation using the line shape from the theory of the line wings (Ref. 15), (3) calculations using Thomas-Nordstorm line shape with the constants chosen for the rotational band, (4) values obtained from field measurements (Refs. 4 and 5), (5) experimental value (Ref. 21), (6) calculations by Ma and Tipping for the water vapor lines broadened by nitrogen.*

The systematic discrepancy between the calculated and measured values makes us to suppose the presence of the unknown factor to cause the absorption. We should like to underline here that is just the transmission windows where this factor produces an essential effect on the radiation absorption by the atmosphere, while being negligibly small within the absorption bands, where, even if it is equal to the experimentally measured continuum. The behavior of the contribution coming from the water vapor in a wide spectral range from 10 to 10000 cm^{-1} is shown in Fig. 5.

The deviation of the calculated and experimental data on the molecular absorption increases with decreasing wavelength, so the question on the origin of the absorption in the visible and near IR region that follows from field measurements is still to be addressed.

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REFERENCES

1. G.L. Stephens and Si-Chee Tsay, Quart. J. Roy. Met. Soc. **116**, 671–704 (1990).
2. K.Ya. Kondrat'ev, V.I. Binenko, and I.N. Mel'nikova, Meteorol. Gidrol. **2**, 14–23 (1996).
3. C. Tomasi, R. Guzzi, and O. Vittori, J. Atmos. Sci. **31**, 255–260 (1974).
4. Yu.A.Pkhalagov, V.N.Uzhegov, and N.N.Shchelkanov, Atmos. Oceanic Opt. **7**, 714–720 (1994).
5. M.V. Panchenko, V.E. Zuev, S.D. Tvorogov, U.N. Uzhegov, L.I. Nesmelova, Yu.A. Pkhalagov, O.B. Rodimova, and N.N. Shchelkanov, *Proc. of the 7th Atmos. Radiat. Measurement (ARM) Sci. Team Meeting,* March (1997).
6. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, Atmos. Oceanic Opt. **10**, 81–83 (1997).
7. R.E. Roberts, J.E.A. Selby, and L.M. Biberman, Appl. Opt. **15**, 2085 (1976).
8. V.N. Aref'ev, Atm. Opt. **2**, No. 10, 878–894 (1989).
9. N.N.Shchelkanov, Yu.A.Pkhalagov, and V.N.Uzhegov, Atmos. Oceanic Opt. **5**, No. 7, 431–434 (1992).
10. M.E. Thomas and C.J. Delaye, in: *Proceedings of the 14th Annual Review Conference on Atmospheric Transmission Models* (1991), 342 pp.
11. M.E. Thomas and R.J. Nordstrom, Appl. Opt. **24**, No. 21, 3526–3530 (1985).
12. S.A. Clough, F.X. Kneizys, and R.W. Davies, Atm. Res. **23**, 229–244 (1989).
13. S.A. Clough, in: *Proceedings of the Third Atmos. Radiation Measurements (ARM) – Science team Meeting* (1993), 11 pp.
14. S.D. Tvorogov and L.I. Nesmelova, Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana **12**, No. 6, 627–633 (1976).
15. L.I.Nesmelova, O.B.Rodimova, and S.D. Tvorogov, *Spectral Line Shape and Intermolecular Iteration* (Nauka, Novosibirsk, 1986) 216 pp.
16. V.V. Fomin, *Molecular Absorption in the Infrared Transmission Windows* (Nauka, Novosibirsk, 1986) 234 pp.

17. Q. Ma and R.H. Tipping, J. Chem. Phys. **96**, 8655–8663 (1992).

18. Q. Ma and R.H. Tipping, J. Chem. Phys. **97**, 818–828 (1992).

19. P.W. Rozenkranz, J. Chem. Phys. **87**, 163–170 (1987).

20. D.E. Burch and R.L. Alt, Rep. AFGL–TR–84–0128 (U.S. Air Force Geophys. Laboratory, Hanscom Air Force Base, Mass, 1984), D.E. Burch, Rep.AFGL–TR–85–0036 (1985), D.E.Burch and D.A.Gryvorak, Rep. AFGL–TR–0054 (1976), D.E.Burch, SPIE Proc. **28**, 28 (1981).

21. S.F. Fulghum and M.M. Tilleman, J. Opt. Soc. Amer. B. **8**, No. 12, 2401–2413 (1991).

22. V.A. Kapitanov, Yu.N. Ponomarev, and I.S. Tyryshkin, Atmos. Oceanic Opt. **10**, No. 12, 928–930 (1997).

23. D.E.Burch, D.A.Gryvnak, R.Patty, and Ch.E.Bartky, J. Opt. Soc. Amer. **59**, No. 3, 267–280 (1969).