

WATER VAPOR ABSORPTION IN THE NEAR INFRARED AND SOME OF ITS GEOPHYSICAL IMPACTS

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Estimates of the upper boundary of the short-wave continuum in the water vapor spectrum show that it is much lower than the empirical atmospheric continuum and it is certainly inadequate for interpretation of the "excess absorption" of radiation in clouds.

1. The problem on anomalous (excess) absorption of the short-wave radiation in clouds is discussed in literature for an appreciable length of time (see, for example, Refs. 1, 2 and references therein). There exist different ideas on the nature and mechanism of this phenomenon. Namely, in Ref. 2 the most probable reasons for the anomalous absorption are assumed to be the effect of multiple scattering of the short-wave radiation in clouds, which is responsible for an increase in the photon free path and, therefore, for the increase of cloud absorptance, and the pollution of clouds by components absorbing the short-wave radiation (especially the carbon black aerosol). Another version of the explanation is the effect of the horizontal transfer in a stochastically inhomogeneous cloud.³ Besides, in Ref. 1 the excess absorption by clouds is treated as a result of water vapor absorption continuum. To describe it quantitatively the procedure is used, which was earlier proposed for application to 3.3–4.2 μm spectral region.⁴

In this paper we estimate the magnitude of the excess absorption based on experimental data⁵ and make an attempt to answer the question if the excess absorption may be conditioned by the line wings of the water vapor.

2. The presence of water vapor absorption continuum in spectral regions free from the absorption bands (atmospheric transmission windows) is well established. Note that it is these spectral regions, that determine to a large extent, the in and out going infrared radiation of the Earth. The detailed review of experimental data on the absorption continuum for most important atmospheric transmission windows and the ways of their account is presented in Ref. 6.

The extensive literature is devoted to the long-wave 8–12 μm transmission window. The major empirical features of the water vapor absorption are well understood, namely, the temperature and pressure dependence of the absorption in the cases of both the broadening by a foreign gas and self-broadening. Though the origin of this absorption was lively discussed for a long time (the hypotheses on the absorption by clusters, dimers, aerosols and spectral line wings were proposed) the fundamental role of the far line wings of the water vapor can presently be considered as an unassailable one.

The region of 3–5 μm is less studied, however, the results available enable one to detect the presence of the continuous absorption and to state that its magnitude is much less than that in the region of 8–12 μm . The weak absorption in the region of 2–2.5 μm was investigated experimentally at high temperatures. If the temperature dependence of the absorption in this region is adopted to be similar to that in the 3–5 μm region, the continuous absorption at room temperature in these regions will be of the same order of magnitude.

Only separate measurements are available in visible and near infrared regions. They show the existence of an absorption and its very small magnitude. So, in Ref. 6 the value of the absorption coefficient $6 \cdot 10^{-10} \text{ cm}^{-1}$ at the frequency $\nu = 9466 \text{ cm}^{-1}$ is given (within the 1 μm window of the water vapor) obtained at partial water vapor pressure $P_{\text{H}_2\text{O}} = 16.5 \text{ Torr}$, the pressure of N_2 as a broadening gas $P_{\text{N}_2} = 1 \text{ atm}$ and the temperature $T = 30^\circ \text{C}$. Hence, it follows that the absorption in the region considered is nearly two orders of magnitude less than that in the region of 4 or 2 μm . Weak water vapor continuous absorption under atmospheric conditions in the 0.648–3.92 μm region is reported in Ref. 5, in which the values of the absorption coefficients in narrow spectral intervals from this region are presented. These values were obtained using a special way of data processing of measurement data on the atmospheric attenuation of solar radiation and are accurate to $\sim 25\%$. Since the absorption coefficients are proportional to the first power of the water vapor pressure they can be considered as being due to broadening by N_2 . We used them to estimate the magnitude of the continuous absorption in the visible and near infrared regions.

3. Absorption coefficient k may be generally presented as a sum of two terms, one of which, k_{sel} , is due to the lines located within the narrow spectral interval or near it ($\Delta\nu \sim 20\text{--}25 \text{ cm}^{-1}$) and the other, k_{cont} , describes the absorption by the wings of more distant lines

$$k = k_{\text{sel}} + k_{\text{cont}} .$$

Since measurements in Ref. 5 are not monochromatic (their resolution is $\sim 3\text{--}5 \text{ cm}^{-1}$) one

needs to operate with the transmission function T

$$T = T_{\text{sel}} T_{\text{cont}},$$

$$T_{\text{sel}} = \frac{1}{\Delta n} \int_{n_1}^{n_2} e^{-k_{\text{sel}}(\nu)w} d\nu = \frac{1}{\Delta n} \sum_j e^{-k_{\text{sel}}(\nu_j)w} d\nu_j,$$

$$T_{\text{cont}} = \frac{1}{Dn} \int_{n_1}^{n_2} e^{-k_{\text{cont}} w} d\nu \approx e^{-k_{\text{cont}} w},$$

where w is the amount of the absorber. The continuous absorption coefficient k_{cont} can be determined from the relations

$$T_{\text{cont}} = T/T_{\text{sel}}; k_{\text{cont}} = -\frac{\ln(T/T_{\text{sel}})}{w} = -\frac{\ln T_{\text{cont}}}{w}.$$

The values T_{sel} were calculated using the database from Ref. 7 and the Lorentzian line shape truncated at $\Delta\nu = 20 \text{ cm}^{-1}$. The calculation quality of T_{sel} was controlled by comparing with experimental data⁸ for several absorption bands, see Fig. 1. Figure 2 depicts the results of calculation of T_{sel} and T as functions of w at several characteristic frequencies using the absorption coefficients from Ref. 5. The coefficients of continuous absorption thus obtained are given in Fig. 3 and in the Table I.

4. Let us consider a possible explanation of the continuous absorption as to be associated with the far line wings of the water vapor.

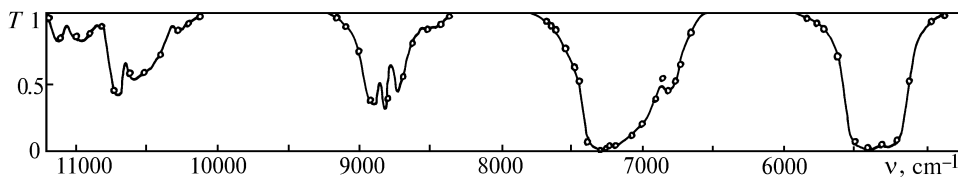


FIG. 1. Transmission functions for the mixture $\text{H}_2\text{O}-\text{N}_2$ at the total pressure $P = 1 \text{ atm}$, $T = 296 \text{ K}$ and the absorber amount $w = 0.845 \text{ g/cm}^2$. The curves are the experimental data,⁸ the circles are the results of the present calculation with the Lorentzian line shape truncated at the distance $\Delta\nu = 20 \text{ cm}^{-1}$ from the line center.

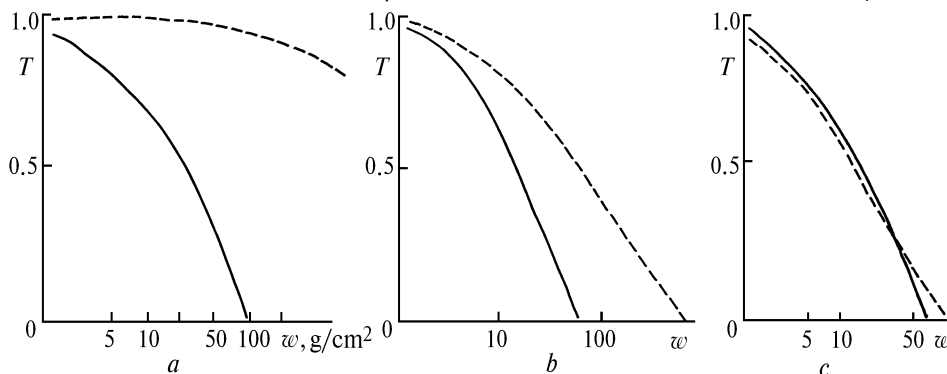


FIG. 2. Transmission functions: T_{exp} calculated using the experimental values⁵ k_{exp} (—), and T_{sel} (---) as functions of the absorber amount w in the following spectral intervals: a) $13243.3-13246.8 \text{ cm}^{-1}$ ($\lambda = 0.755 \text{ }\mu\text{m}$); b) $12344-12347 \text{ cm}^{-1}$ ($\lambda = 0.81 \text{ }\mu\text{m}$); c) $10988-10990 \text{ cm}^{-1}$ ($\lambda = 0.91 \text{ }\mu\text{m}$).

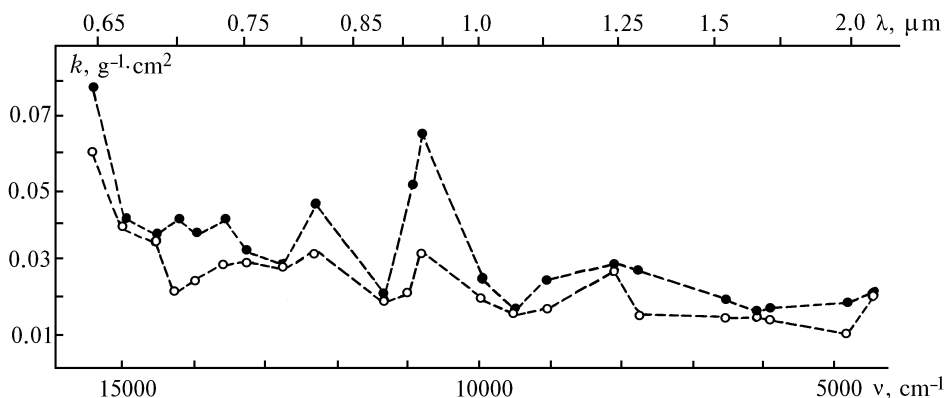


FIG. 3. Absorption coefficients: k_{exp} (Ref. 5) (\bullet) and $k_{\text{cont}} = -(\ln(T_{\text{exp}}/T_{\text{sel}}))/w$ (\circ).

The fact that the contour of the vibration-rotation lines far from their center deviates from the

Lorentzian shape can be thought as well-established. The main features of the absorption behavior at the

line periphery are well understood, namely, the near wings may be somewhat higher than Lorentzian ones and at large frequency shifts the exponential decay should develop. Such a behavior of the line contour is evident from the analysis of the extensive ensemble of experimental data on molecular absorption of NH_3 , HCl , CO_2 , H_2O , etc.

TABLE I. Calculated and measured coefficients of continuous absorption, $\text{g}^{-1} \text{cm}^2$.

λ , μm	k_{exp} [5]	k_{cont}	$k_{\text{cont Lor}}(\Delta\nu = 500 \text{ cm}^{-1})$
2.27	0.021	0.02	0.001
2.12	0.018	$8 \cdot 10^{-3}$	$3 \cdot 10^{-3}$
0.91	0.052	0.026	$7.7 \cdot 10^{-4}$
0.81	0.046	0.03	10^{-4}
0.755	0.032	0.03	10^{-6}

Theoretical studies result in exponential decay in the far line wings as well. The cause of this effect lies in the character of the intermolecular interaction at small intermolecular distance and in the decisive role of this interaction in the line shape formation.^{4,9,10} The detailed calculations of the line contour of water vapor for the bands in the visible and near infrared spectral regions are rather cumbersome. Therefore, it is worth making some preliminary estimates.

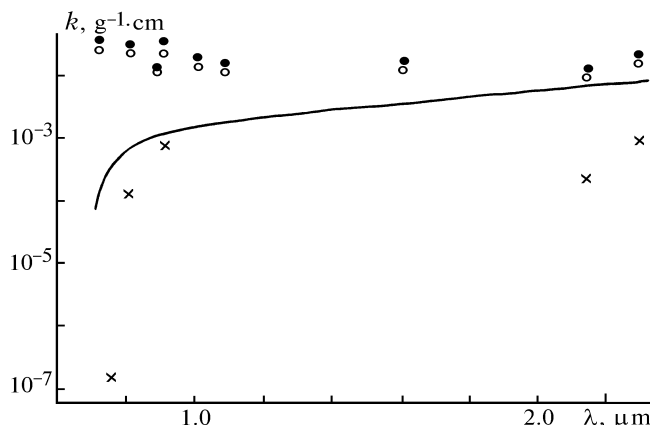


FIG. 4. Absorption coefficients: (Ref. 5) k_{exp} (\bullet), $k_{\text{cont}} = -(\ln(T_{\text{exp}}/T_{\text{sel}}))/w$ (\circ), $k_{\text{cont Lor}}(\Delta\nu = 500 \text{ cm}^{-1})$ (\times) and the continuous absorption coefficient from Ref. 1 (—).

We have calculated the absorption coefficient of the water vapor for lines with Lorentzian line shape broadened by N_2 k_{Lor} truncated at $\Delta\nu \cong 500 \text{ cm}^{-1}$. Since the deviations of the line contour from the Lorentzian one in favor of the exponential decay are found at the frequency shifts less than 500 cm^{-1} (see, for example, Ref. 4, Fig. 4 and Ref. 10, Fig. 1) the values obtained can be considered as the upper boundary of the absorption coefficient.

The values k_{Lor} given in the table and in Fig. 4 evidently show that the calculation even with the Lorentzian wings results in the absorption coefficient

significantly smaller than the experimental one. It immediately follows herefrom that it is necessary to seek other causes of the continuous attenuation in the spectral region under consideration than the line wing absorption of the water vapor in the visible and near infrared spectral regions.

Of course, some refinements of the figures should necessarily appear in calculations with actual line shapes, taking additionally in account specific features of the short-wave spectral region. However, this will hardly affect the general conclusion drastically.

5. The results of the present estimates illustrate the long-discussed problem on the existence of the "atmospheric continuum," whereas the continuum due to the molecular absorption can be named "spectroscopic continuum." Now, the cloudless atmosphere is kept in mind and the atmospheric continuum is often attributed to the submicron aerosol (therefore the corresponding attenuation coefficient is proportional to the absolute humidity but not to the relative one, as it is for the coarse-disperse aerosol). The fact that the atmospheric continuum is stronger than the spectroscopic continuum follows from the figures presented. Here, we are dealing with the transmission microwindows, i.e., the spectral intervals free from strong absorption lines.

One can say about the "cloud continuum" as well, which is a factor appealed for to clarify the "radiation paradox." The paradox consists in the fact that the sum of the reflection and transmission coefficients of solar radiation by a cloud layer is less than unity. Though the estimates of the cloud continuum appear to be lower than those of the atmospheric continuum (it is interesting by itself) nevertheless the first is higher than the upper boundary of the spectroscopic continuous absorption.

REFERENCES

1. G.L. Stephens and Si-Chee Tsay, *Quart. J. Roy. Meteorol. Soc.* **116**, 671–704 (1990).
2. K.Ya. Kondrat'ev, V.I. Binenko, and I.N. Mel'nikova, *Meteorol. Gidrol. No. 2*, 14–23 (1996).
3. G.A. Titov, *Atm. Oceanic Opt.* **9**, No. 10, 825–838 (1996).
4. S.A. Clough, F.X. Kneizys, and R.W. Davies, *Atmospheric Research* **23**, 229–241 (1989).
5. C. Tomasi, R. Guzzi, and O. Vittori, *J. Atmos. Sci.* **31**, 255–260 (1974).
6. M.E. Thomas and C.J. Delays, in: *Proceedings of the 14th Annual Review Conference on Atmospheric Transmission Models*, 11–12 June (1991), pp. 342–349.
7. L.S. Rothman, R.R. Gamache, R.H. Tipping et al, *J. Quant. Spectrosc. Radiat. Transfer* **48**, 469 (1992).
8. J. Jamanouchi and M. Tanaka, *J. Quant. Spectrosc. Radiat. Transfer* **34**, 463 (1985).
9. L.I. Nesmelova, O.B. Rodimova, and S.D. Tvorogov, *Spectral Line Shape and Intermolecular Interaction* (Nauka, Novosibirsk, 1986), 216 pp.
10. Q. Ma and R.H. Tipping, *J. Chem. Phys.* **97**, No. 2, 818 (1992).