Contribution of weak water vapor lines to attenuation of shortwave radiation

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The contribution of weak water vapor lines, which are usually neglected in estimates of solar radiation attenuation in the atmosphere, to the total atmospheric absorption in the near infrared and visible regions is studied. Calculations are based on the HITRAN–96 and "globalB *ab initio* results [H. Partridge and D. Schwenke, J. Chem. Phys. **106**, 4618–4639 (1997)]. It is found that the additional absorption amounts to 2–4% of the overall water vapor absorption for horizontal paths of different length, and it is most significant in the visible spectral region.

Introduction

In recent years an increasing number of studies are devoted to the problem of the radiative balance of the atmosphere and the role of weak absorption effects connected, in one way or another, with atmospheric water vapor.[1–3] The problem is that there is a considerable discrepancy between the calculated and measured radiative budget of the Earth even in the clear cloudless atmosphere with the measured value of the atmospheric absorption exceeding the calculated one (see, for example Refs. 2 and 3). As is indicated in Ref. 2, this excess absorption correlates with the water vapor concentration, however it does not correlate with cloudiness. Different hypotheses are invoked to explain this discrepancy. For instance, in Ref. 1 the excess absorption in clouds is explained by the fact that no proper account is taken of the dispersion effects in the models used. In Ref. 2 it is shown that the continuum absorption can essentially contribute to the calculated integral absorption. In Ref. 3 the hypothesis is put forward that weak lines neglected in the HITRAN and GEISA databases can give an additional contribution to the total water vapor absorption in the near infrared and visible regions.

In this paper the contribution of weak water vapor absorption lines to the total atmospheric absorption in the 7000–18000 cm^{-1} region is directly calculated. The main idea, as in Ref. 3, is that the number of weak lines considerably exceeds that of strong lines, hence their total contribution may be noticeable. However, contrary to Ref. 3, where the number and intensities of weak lines were interpolated from the HITRAN–96 data, we use the spectral data (line positions and intensities) obtained on the basis of high-accuracy *ab initio* calculation.[4] This allows more precise evaluation of the role of weak lines.

Spectral line parameters and the method for calculation

The HITRAN–96 spectral database, which is acknowledged as most widely used for atmospheric applications, contains 15803 lines of the $H_2{}^{16}O$ molecule in the 7600–18000 cm^{-1} spectral range with the intensities exceeding the 10^{-27} cm/mol. Besides, lines of the $H_2{}^{17}O$ and $H_2{}^{18}O$ isotopic species are partly included in it.

The database obtained on the base of Partridge and Schwenke's high-accuracy *ab initio* calculations of the H_2O intramolecular potential and dipole moment functions and variational calculations of the rovibrational energy levels, transition frequencies, and intensities[4] contains considerably more lines as compared with the HITRAN–96 database. In particular, in accordance with Ref. 4, there are more than 400 000 lines with the intensities exceeding 10^{-30} cm/mol in the same 7600–18000 cm^{-1} region. Note also, that in the 12900–14300 cm^{-1} region the number of lines with intensity less than 10^{-26} cm/mol exceeds 19 500, while the total number of lines with intensity 10^{-30}–10^{-23} cm/mol is 21 800. As an example, the HITRAN–96 database contains only 2100 lines in the same region, while the number of lines with intensity less than 10^{-26} cm/mol does not exceed 200. The database from Ref. 4 includes lines of hot bands and high overtones of bending vibrational modes, as well as absorption lines of the isotopic species of the water molecule.

The accuracy of line positions and intensities in Ref. 4 is high enough to perform the estimations. The root-mean-square deviation of the calculated line positions from those presented in the HITRAN–96 does not exceed 0.1 cm^{-1}, while the rms deviation of the integral intensities of bands is of the order of 20%. Note

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that the calculated line positions in Ref. 4 were corrected by the fit of parameters of the potential function to the HITRAN–96 data (30092 lines), whereas the intensities were obtained on the basis of *ab initio* calculations alone.

The line halfwidths induced by air pressure were taken to be an average for a given rotational quantum number J of the lower state. The halfwidth of lines with $J > 12$ was taken to be of 0.005 cm^{-1}/atm.

The absorption function with the 20 cm^{-1} resolution was calculated by the direct line-by-line method[5] taking into account the absorption by three water vapor isotopic species. The line profile was assumed to be Lorentzian; the profile was cut off at the 25 cm^{-1} detuning from the resonance frequency. The continuum absorption was ignored. The AFGL model was used in calculations for the tropical latitudes.[6] The horizontal path at the zero height was chosen so that the m_2n absorbing mass was close to that on an inhomogeneous path passing through the entire atmosphere at angles of 0°, 60°, and 70°.

Calculated results and their discussion

Lines with different intensities may be considered as weak in different cases depending on the region under study and on whether the corresponding data are included in the HITRAN–96 database. So, to evaluate the role of weak lines, we first selected the strong lines contained in the Partridge and Schwenke's database in such a way that their number was the same as in the HITRAN–96. In this case the absorption at weak lines was considered as a difference between the total calculated absorption and that resulting from the strong lines only. The calculations were carried out for the 7000–18000 cm^{-1} spectral region. The results are presented in Figs. 1–4.

The calculations have shown that weak water vapor lines give a contribution of 2–4% to the integral absorption on the horizontal paths 2.1 to 6.2 km long. This additional contribution is sufficiently large, and it cannot be neglected when evaluating the integral absorption of the solar radiation by the atmosphere.

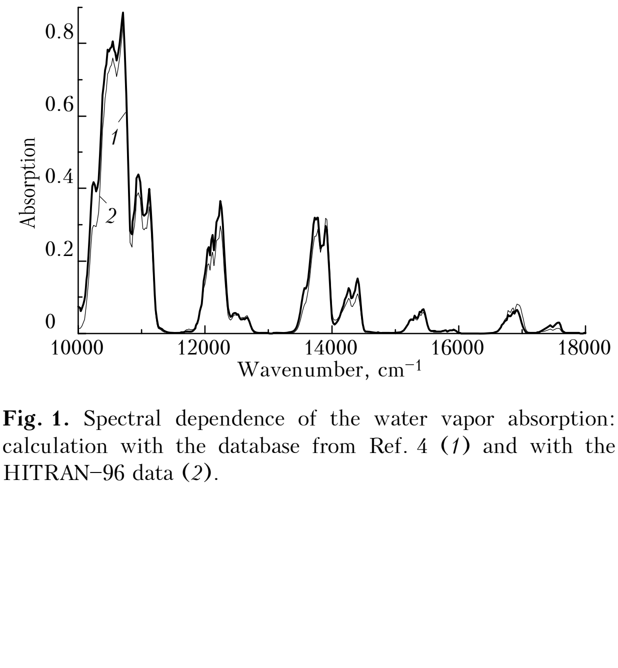

Fig. 1. Spectral dependence of the water vapor absorption: calculation with the database from Ref. 4 (*1*) and with the HITRAN–96 data (*2*).

Note (see Fig. 1) that for some spectral ranges, for example, for the 10300 cm^{-1} region the difference is large enough – the absorption increases from 0.3 to 0.4. It likely indicates the necessity of refining and complementing HITRAN–96, as well as calculating more precisely the intensities of weak lines. Obviously, such calculation should take into account all the complexities in the H_2O intramolecular dynamics.

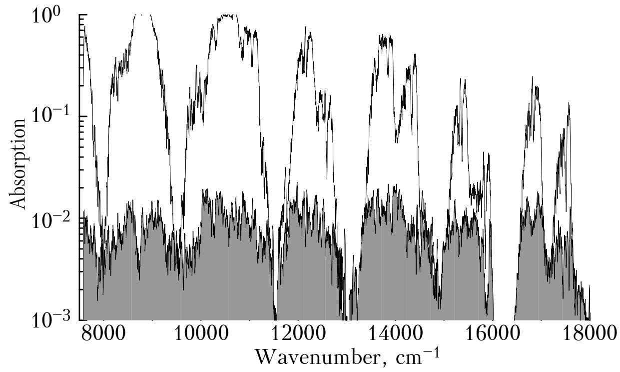

Fig. 2. Spectral dependence of the H_2O absorption. The dashed area correspond to the contribution of weak lines.

The calculated results on absorption of shortwave radiation by the water vapor in the 7600–18000 cm^{-1} region obtained with the data from Ref. 4 are presented in Fig. 2. The contribution of weak lines is indicated as dashed areas. It can be seen that contribution of the weak part of the water vapor absorption spectrum is, as a rule, of several percent. However, its relative contribution is large enough in the area of weak absorption bands. The spectral dependence of the absorption by only weak lines, as well as its relative role in the 8000–26000 cm^{-1} region is shown separately in Fig. 3 for three different atmospheric paths. It can be seen, that the relative contribution of weak lines grows rapidly toward the visible spectral region. Moreover, the absorption strongly depends on the path length.

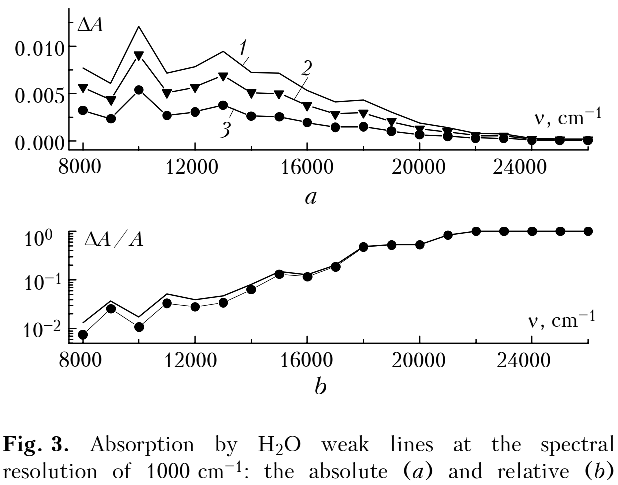

Fig. 3. Absorption by H_2O weak lines at the spectral resolution of 1000 cm^{-1}: the absolute (*a*) and relative (*b*) values of absorption. Curves *1*, *2*, and *3* correspond to the horizontal paths of 2.1, 4.2, and 6.2 km.

It should be noted that the role of weak lines in the atmospheric absorption grows due to the more rapid increase of their contribution with the path length. As an example, the dependences of absorption by weak (curve *1*) and strong (curve *2*) lines on the path length L in the 10000–13000 cm^{-1} region are shown in Fig. 4. As is well known, the absorption by strong lines increases proportionally to $L^{0.5}$, whereas the absorption by weak lines proves to be directly proportional to the path length. Thus, the contribution due to weak lines can be relatively large on long horizontal paths.

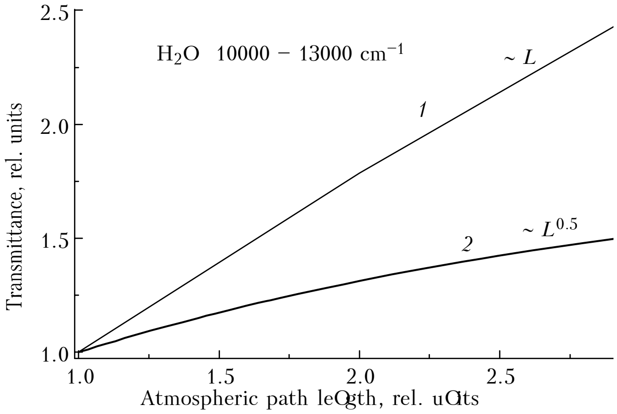

Fig. 4. Absorption as a function of the path length.

The calculations performed allows the following conclusions. First, the water vapor absorption due to weak lines can give noticeable increase in the total absorption, and it should be taken into account when evaluating the radiative balance along with other factors such as continuum absorption, absorption by water dimers, etc. Second, the relative contribution of weak lines depends on the spectral region and on the type and length of an atmospheric path. The largest contribution of weak lines should be expected on the long horizontal paths.

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