Absorption of solar radiation by water vapor: possible causes of anomalous absorption

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Recent publications concerning the so-called anomalous absorption of solar radiation in the atmosphere and the possible contribution of water vapor to this effect are briefly analyzed. The estimates presented show that uncertainty in current knowledge of the initial water vapor spectroscopic parameters, including water dimer hypothesis, can contribute only a small fraction of the recently revealed anomalous absorption of solar radiation in the atmosphere.

Introduction

About 8–9 years ago first papers appeared describing the so-called anomalous absorption in atmosphere.^{1–5} It was found that models systematically underestimate the value of absorbed solar flux compared to experiments. Disagreement in the global mean (GM) flux reached 25 W/m², which is ~30% of the total absorption of solar radiation in the atmosphere (~80 W/m²). In spite of numerous efforts undertaken during past years, no definite

answer has been obtained to the question on the cause of the disagreement. Moreover, there is evident decline of the number of "anomalous absorption works" in recent years. A number of possible causes explaining the anomalous absorption have been put forward; however, as far as this effect was noticed even for clear-sky conditions,⁶ the "main suspects" was aerosol and water vapor. The water vapor absorption (see Fig. 1) dominates absolutely over all other gases in the solar spectral region, causing more than 90% of the total short-wave absorption in the atmosphere.



Fig. 1. Water vapor contribution to the absorption of solar radiation in the atmosphere: Optical depth of the vertical atmospheric layer 0-50 km for the total water vapor absorption, for water vapor continuum separately and for other atmospheric gases (*a*); Direct solar flux at the surface. The dashed line shows the flux at the top of the atmosphere (*b*).

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In this paper we analyze recent theoretical and experimental works aimed at estimating possible water vapor contribution to the anomalous absorption. Under the term "anomalous absorption" (AA) we mean here not only possible *real* absorbers of radiation in the atmosphere not accounted for to date, but also uncertainties in calculations of the absorbed solar radiation caused by various factors.

The problem of anomalous absorption

The survey of recent papers reveals significant disagreement in both the question on possible contribution of water vapor to the AA and on the value of AA itself. Conditionally, these papers can be divided into three groups.

1. Arking in his papers^{2,6} reported on a significant AA (17–28 W/m² GM flux) detected and about strong correlation of the absorption with water vapor column density. This fact can point to the water as a main source of AA. Similar correlation also was found in Refs. 1, 4, and 7.

2. In other group of papers, (see Refs. 5 and 8) the authors report much lower value of AA (for example, less than 7 W/m^2 GM flux in Ref. 5) and the absence of any correlation with water vapor content.

3. Finally, in the third group of papers, (for example, Refs. 9 and 10) authors have not detected any AA within the accuracy of their experiment (~5 W/m²). However, one circumstance should be taken into account that distinguishes these works (as well as some works from the group 2) from the papers of the first group. The authors compare measured flux with the calculated one that has already been preliminary fitted to the measured flux by varying some parameters of their aerosol (in Ref. 9) or aerosol and continuum model (in Ref. 10). In other words, in the papers of the group 1 the comparison was made between experiment and model, while in the group 3 the comparison has been done between the experiment and model fitted to the experiment. It is obvious that in such an approach any AA that has spectral dependence smooth enough, especially one similar to the aerosol, may be partly or in some cases completely included in the fitted aerosol model parameters, even if the AA is not caused by aerosol absorption.

Thus, such an approach is justified only in the cases where we are absolutely sure that AA is caused by an incomplete inclusion of aerosol or the AA has spectral dependence very different from the one for aerosol (or for another model, parameters of which are fitted). It is possible that this fact – the general fitting of the unknown model parameters – explains partly the decrease in the number of recent papers where a significant AA is reported. Some confirmation of this idea can be found for example in Ref. 10, where authors report about significant disagreement between the measured and "initially" calculated data, but after fitting the parameters of

water vapor continuum model the disagreement became negligible.

Uncertainties in the calculation of H₂O absorption

One of the possible causes of the disagreement in the value of AA reported by different investigators is the uncertainty in the knowledge of the initial spectroscopic parameters of water vapor. The use of different models of continuum absorption or different databases of spectral line parameters may lead to different results. The possible sources of the uncertainty in the initial spectroscopic information and their impact on calculated solar flux absorbed in the atmosphere have been discussed for example in Refs. 11 to 17 and in some recent papers as well. Below we present some brief analysis of these works.

1. Permanent update of the HITRAN database, the most widely used database of spectral line parameters today, leads to that different HITRAN versions are used by different research groups. It is sufficient to point out that six versions of the HITRAN database were issued during the period from 1992 to 2004: HITRAN-92; HITRAN-96; HITRAN-96 with Giver et al. corrections¹⁸ (or HITRAN-99); HITRAN-2000 (or HITRAN-2k), HITRAN-2001 (or HITRAN v.11.0) update¹⁹ for some molecules including H₂O and HITRAN-2004 (or HITRAN v. 12.0).

It was shown in Refs. 13 and 15 that the maximum disagreement between the calculated solar flux at surface appears in the cases of using HITRAN-96 and HITRAN-2001 databases that reaches ~0.8 W/m² for solar zenith angle of 30° and mid-latitude summer, which corresponds to ~0.27 W/m² of GM flux.

2. The continuum absorption by water vapor is among most often discussed possible causes of AA.⁶ In addition to the fact that the nature of continuum absorption does not have yet a unique explanation itself and several different approaches exist to solution of the problem, there is also significant quantitative difference even between various versions of the same continuum model – CKD-model²⁰ (Clough, Kneizys, Davies), most widely used today in radiative transfer codes. The situation with the updates of the CKD continuum model is even more complicated than with the HITRAN database. Eight different versions of the CKD-model were issued during the last eight years. The estimated^{13,15} difference between GM solar flux absorbed in the atmosphere as calculated by two recent versions of CKD continuum reaches up to 0.9 W/m^2 or 1.1% of the total absorption of solar radiation in atmosphere.

3. Another possible source of disagreement between different radiative transfer assessments is the absorption within weak lines of Partridge– Schwenke^{21,22} that may be accounted for or not. It was shown in Refs. 13 and 15 that the neglect of these lines leads to an underestimation of the calculated GM solar flux absorption up to $0.9~W/m^2.$ This result is also in a good agreement with the assessments obtained in Refs. 11 and 12.

4. In spite of the above mentioned regular update of the HITRAN database there remain questions about the quality of water vapor line parameters in the bands 2ν (7100 cm⁻¹), $2\nu + \delta$ (8800 cm^{-1}) , 3v (10600 cm⁻¹), $3v + \delta$ (12200 cm⁻¹), and 4ν (13800 cm⁻¹). An alternative to the HITRAN database of H₂O spectral lines (the so-called ESA database), reported in Refs. 23 and 24, shows essentially stronger absorption by water vapor in the bands $2v + \delta$, 3v, $3v + \delta$ and 4v (by 38, 6, 15 and 10%, respectively, as compared with that following HITRAN-99 (see Ref. 25)). In spite of numerous criticism of the ESA database the measurements repeated at Rutherford Appleton Laboratory (UK) in the 2ν and 2ν + δ water vapor absorption bands have confirmed the presence of extra absorption compared to that calculated by HITRAN-2000 (by 12 and 15%, respectively¹⁴), though much less for the $2v + \delta$ band than was claimed initially in Refs. 23-25. The independent measurements performed in Ref. 26 also show an 8% higher absorption, on the average, compared to that by HITRAN-2000 in the spectral region 5800–7900 cm^{-1} .

An assessment of additional contribution to absorption of short-wave radiation due to the discussed correction to HITRAN database gives the global mean values $1.1-1.5 \text{ W/m}^2$ (see Refs. 12, 14, and 15).

5. One more possible source of the AA caused by water vapor could be the absorption by water clusters. The subject of water clusters and their role in the atmospheric radiative budget has undergone a rebirth in recent years.^{27–29} However, in spite of numerous theoretical and experimental investigations of the simplest water cluster – water dimer,^{30–33} the first reports³⁴ about detection of the absorption by dimers in the atmosphere (in spectral region near 13300 cm⁻¹) and in the equilibrium laboratory conditions¹⁷ (near 5230 cm⁻¹) have appeared only recently.

Quantitative assessments of the possible water dimer contribution to the absorption of solar radiation have been made in Refs. 16, 17 and 30. These assessments are, in general, in a good agreement with each other and give the value of extra absorption from 0.6 to 1.5 W/m^2 of GM flux, depending on the width of the water dimer absorption bands, which is still a very uncertain parameter and can vary from 6 to 100 cm⁻¹ for different dimer bands.³⁰

Conclusions

All possible sources of errors in the calculation of solar absorption in the atmosphere discussed above, caused by uncertain knowledge of water vapor parameters, are presented in the summary table. It can be seen from the table that the maximum inaccuracy due to all mentioned factors can reach $4-5 \text{ W/m}^2$ of GM flux or 5-6% of the total shortwave absorption in the atmosphere, which is undoubtedly big value. However, this inaccuracy cannot explain AA of $17-25 \text{ W/m}^2$ that was reported in the works by Arking and others for clear sky. Most likely, such AA has been caused by the combination of many factors, including those discussed in our work and others like the error in accounting for aerosol absorption, calibration inaccuracy, and so on.

Table. Possible errors in calculation of the absorption
of short-wave radiation in the atmosphere caused by
uncertainties in the initial spectroscopic information on
water vapor. Spectral region 2 500–20 000 cm ⁻¹
(0.5-4 um)

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Source of uncertainty	Error in flux (GM), W/m ²	Part of the total atmospheric absorption, %	References
HITRAN-2001–HITRAN-96 HITRAN-2001–HITRAN- 2000	0.27 0.2	0.4 0.3	13, 15
CKD 1 – CKD 2.4 (continuum) Partridge-Schwenke weak	0.9	1.1	13, 15
lines	0.9	1.1	12, 13, 15
ESA correction to HITRAN	1.1 - 1.5	1.4 - 1.8	12, 13, 15
Water dimer absorption	0.6 - 1.5	0.8 - 1.8	17, 30, 34
Total:	3.8-5.1	4.8 - 6.2	

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