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SPECTROSCOPY OF AMBIENT MEDIUM

Water Vapor Continuum Absorption in Near-IR Atmospheric Windows

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Abstract—The near-infrared water vapor absorption is measured in the 2000–8000 cm^{-1} spectral region. Spectra were recorded using an IFS 125 HR Fourier spectrometer at a temperature of 287 K and a spectral resolution of 0.03 cm^{-1}. The water vapor continuum absorption spectrum is retrieved using the known absorption in the 2500 cm^{-1} region as a reference point. It is shown that the continuum absorptions in four windows differ by no more than 20% under investigation conditions. This contradicts the MT_CKD continuum model, which predicts a much stronger variability of the continuum in these windows.

Keywords: H_2O continuum, MT_CKD continuum, atmospheric windows, FTS spectroscopy

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INTRODUCTION

Water vapor is one of the most important gases for the radiation balance of the Earth's atmosphere, which plays the role of a positive feedback in climate change [1]. The infrared spectrum of water vapor includes both strong absorption bands, consisting of a large number of individual spectral lines, and absorption windows, located between them, where the absorption is rather weaker. In these windows, the radiation absorption is conditioned, mainly, not by spectral lines, but by the so-called water vapor continuum, i.e., the absorption component, which weakly depends on the frequency, is present in both absorption bands and transparency windows, and strongly affects the radiation balance of the atmosphere and remote sensing [2–4].

The nature of the water vapor continuum absorption is a matter of much discussion. There are three principal hypotheses: cumulative contribution of far wings of water molecules [5, 6], absorption by stable and metastable water dimers (i.e., by pairs of weakly bound water molecules) [7–11], and collision-induced absorption, understandable as transitions induced by short-term guided/changed dipole moment at the instant of collision [12]. Two components of the continuum absorption are distinguished: self-continuum, conditioned only by water molecules, and foreign continuum, conditioned by interaction of water molecules with molecules of other gases in the Earth's atmosphere, mainly, with nitrogen. In this paper, we study the self-continuum, which gives the decisive contribution in the radiation absorption in atmospheric transparency windows.

Most of the programs for the calculation of radiation propagation in the atmosphere use today the semi-empirical continuum model MT_CKD [13], which rather adequately describes the continuum absorption in many spectral intervals. However, it is based on the fitting to a limited amount of experimental data (mainly, in far-infrared spectral region) and is an extrapolation in almost all near-infrared and visible regions. Moreover, as recent measurements have shown [14], even in the spectral region where the model has been fitted to the experiment, it significantly (up to 50%) deviates from new data found at other temperatures. Thus, the predictability of this model in certain spectral intervals leaves something to be desired. Physical consideration of the continuum, postulated within the CKD/MT_CKD model, also experienced significant changes during two past decades [13] and was under active discussion [8–11, 15].

Many series of experiments were conducted during past years on retrieval of water vapor continuum absorption in a wide spectral range at different pressures and temperatures. These investigations, including those made within the CAVIAR consortium (http://www.met.reading.ac.uk/caviar), have shown the rather complex nature of the continuum with evident arguments in favor of the dominating contribution of water dimers in absorption bands [8, 10, 11]. Unexpectedly, the self-continuum [16, 17] and foreign-continuum [18, 19] absorptions were found to be up to an order of magnitude stronger than in the MT_CKD model in certain transparency windows [13]. Most of these measurements, however, were made at increased pressures/temperatures (in order to detect the weak

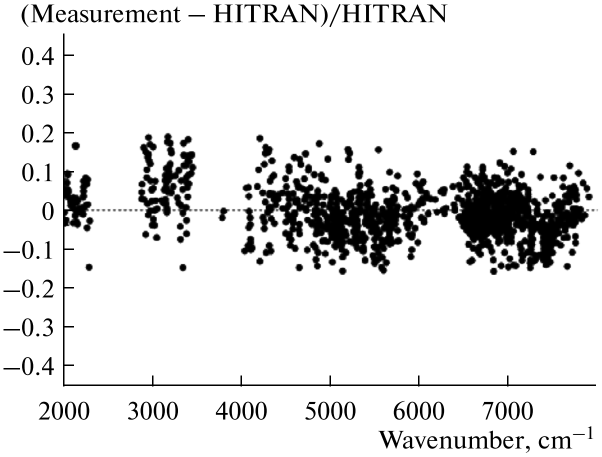

Fig. 1. Relative deviations of experimentally derived water vapor line intensities from corresponding values in HITRAN-2012 [24]. Only relatively strong lines with the error index in HITRAN no less than 5 were considered.

continuum absorption), which makes it difficult to use the data for the Earth's atmosphere. In addition, absorption magnitudes found experimentally in the transparency windows 4700 and 6300 cm^{-1} (2.1 and 1.6 mm) at room temperature turned out to be rather contradictory. Data of [16] and [20], where the Fourier spectroscopy and large cells were used, agree. However, results found in [21] and [22] by methods of calorimetric interferometry and cavity ring-down spectroscopy, respectively, testify to significantly lower self-continuum magnitudes, which also differ from each other by a factor of 4–5.

We have conducted measurements similar to those conducted earlier in [20]. For more reliable recording of the weak continuum absorption in transparency windows, the experimental setup was upgraded; in particular, the optical path length in the multipass cell was increased 1.75 times.

EXPERIMENT

The experiment was conducted using a high-resolution Fourier spectrometer Bruker IFS-125 FTS and a 30-m base-length White multipass cell at V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences (http://www.iao.ru/en/resources/equip/cells). The schematic view of the Fourier spectrometer and description of its elements, including the multipass cell, were given earlier in [20, 23]. To record more reliably the weak water vapor continuum absorption in transparency windows, the optical path length in the experimental cell was increased from 612 [20] to 1065.5 m due to installation of new silver-coating mirrors. Focal lengths of these mirrors were the same as of the preceding ones; therefore, the optical system for the Fourier spectrometer synchronization with the cell was the same [20, 23]. New mirrors were larger in geometrical sizes: the diameter of the objectives of the two back mirrors was 30 cm, the input front mirror was 50 × 30 cm (i.e., by 1.67 times longer than the preceding one [23]). The reflection coefficient of the silver-coated mirrors in the near-infrared range exceeded 0.98 (for comparison: the reflection coefficient of the aluminum-coated mirrors used earlier was approximately 0.87).

Before any measurements, the cell was evacuated to a pressure of 0.02 mbar, the transmission spectrum of the evacuated cell was used as a baseline. The measurements were conducted at a temperature of 287 K and a water vapor pressure of 12.4 mbar in the region 1800–10000 cm^{-1} with a spectral resolution of 0.03 cm^{-1}. As the radiation source, an Osram halogen lamp with a power of 50 W was used. The signal, after passing through the cell, was recorded by a liquid-nitrogen-cooled InSb radiation detector. The pressure in the cell was measured with a MKS Baratron sensor, having an error of 0.25%. When measuring in the cell with water vapor, however, it is important to exclude the systematic error, which can be conditioned, for example, by the adsorption and desorption of water vapor on the cell walls during the experiment, as well as inhomogeneous vapor distribution over the volume of the 30-m cell. Therefore, the sensor-measured pressure was then verified by the comparison of intensity magnitudes of the best studied spectral lines from the HITRAN-2012 database [24] with measured intensities, which allowed us to guarantee the water vapor concentration accuracy of no worse than ~3% (Fig. 1).

PROCESSING OF THE EXPERIMENTAL SPECTRA. THE BASELINE

The optical depth τ_m was calculated from the absorption spectra measured in the standard way:

$$\tau_m(\nu) = -\ln\{I(\nu)/I_0(\nu)\}, \qquad (1)$$

where I is the measured intensity of radiation passed through the cell filled with water vapor, I_0 is the same intensity for the empty cell, and ν is the wavenumber, cm^{-1}. The optical depth of the continuum absorption τ_c was derived in transparency micro-windows (i.e., between absorption lines) by the method similar to that used in the MT_CKD model [13] (see also [16]):

$$\tau_c(\nu) = \tau_m(\nu) - \sum \tau_{\text{line},i}(\nu - \nu_i), \qquad (2)$$

where $\sum \tau_{\text{line},i}(\nu - \nu_i)$ is the local Lorentz contribution of H_2O lines centered at ν_i, calculated within 25 cm^{-1} from their centers and excluding the "plinth" (constant magnitude of the absorption, which a Lorentz contour has at a distance of 25 cm^{-1} from the line center). Figure 2 shows the example of such retrieval in a narrow spectral interval.

The local contribution of spectral lines was calculated using the *line-by-line* program [25] and UCL

(University College London, UK) compilation of parameters of water vapor spectral lines [26]. This compilation includes both relatively strong lines from the HITRAN database [24] and more than million weak H_2O lines found from theoretical calculations. As is shown, for example, in [16], the neglect of water vapor weak lines can result in noticeable (by tens of percent) overestimation of the retrieved continuum in transparency windows of 1.6 and 1.25 mm at temperatures higher 400 K. For room temperature, considered in this paper, the impact of weak lines is essentially lower due to a strong positive temperature dependence of their intensities.

Further, the cross-section of the continual absorption ($\mathrm{cm^2\,mol^{-1}\,atm^{-1}}$) was calculated in the standard way:

$$C_s(\nu, T) = \frac{\tau_c(\nu)}{\rho_s P_s L} \equiv \tau_c(\nu)\frac{kT}{P_s^2 L}, \qquad (3)$$

where ρ_s and P_s are the concentration of water molecules and water vapor pressure, respectively; k is the Boltzmann constant; T is the temperature; and L is the optical path length. The absorption cross-section, determined in such a way, is expressed in $\mathrm{cm^2}$ per absorbing molecule and per one atmosphere total pressure at temperature T. It should be remembered that for transformation of these units to those accepted in the MT_CKD model [13] ($\mathrm{cm^2\,mol^{-1} \equiv cm^{-1}(mol/cm^3)^{-1}}$, where the concentration of molecules is normalized to standard conditions, i.e., to a pressure of 1 atm at a temperature of 296 K), $C_s(\nu, T)$ should be multiplied by $T/296$.

The precise accounting for the local contribution of spectral lines is important for retrieval of the water vapor continuum in absorption bands, where many strong lines are located. In transparency windows, which are of interest for the considered investigation, the accuracy of baseline determination (i.e., the level of "zero" absorption/attenuation) becomes the most important factor for the continuum retrieval. Though "zero" attenuation (any attenuation not related to the water vapor absorption) should be taken into account in Eq. (1) through division by the intensity of radiation passed through the empty cell, this does not always "work" in practice. For certain reasons, the baseline in the cell filled with the gas can differ from that in the empty cell. This may be due to variations in the radiation source intensity, a change in the beam path in the multipass cell, and some other causes.

In order to solve this problem, a "reference" point should be set in the spectrum, where the measured absorption could be tied to a known value. As the reference point, we can consider a fragment of the spectrum, where the absorption is close to zero. In this case, the signal generated while radiation is passing through the cell filled with a gas under study is "scaled" (multiplied by a constant usually close to 1) for its coincidence with the signal from the empty cell in the given fragment of the spectrum. For example, in [16, 19, 20] the 9600 $\mathrm{cm^{-1}}$ region of the transparency window was used for such "tie-in", where the expected water vapor absorption (determined by the continuum in the transparency window) should be lower than the sensitivity of the experimental setup.

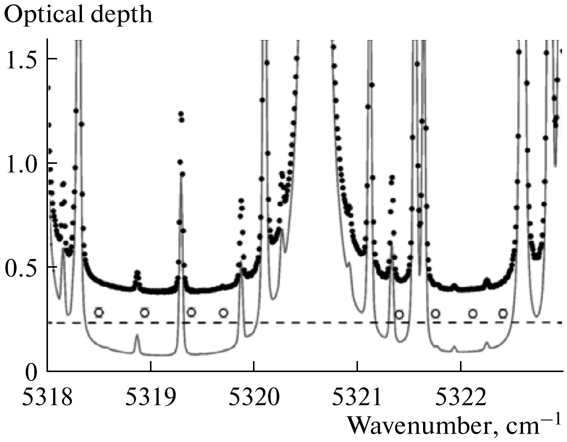

Fig. 2. Example of the measured absorption (points) in pure water vapor and calculated contribution of spectral lines (gray curve) neglecting the continuum (the pressure is 12.4 mbar, the path length is 1065.5 m, the temperature is 287 K). The continuum retrieved in micro-windows (circles) is with the MT_CKD-2.5 model [13] (dashed line).

However, a series of works were published in past years, pointed that the actual continuum can significantly exceed predictions of the MT_CKD model in all transparency windows of the near-infrared region [12, 16–20]. Thus, it is possible to assume that the absorption in the 9600 $\mathrm{cm^{-1}}$ window also can be comparable with the sensitivity threshold for spectrometers with multipass cells, the path length of which is about 1000 m. Therefore, a window of 2500 $\mathrm{cm^{-1}}$ was taken as a reference point in this work, where, as opposite to other windows of the region under study, the continuum absorption is known today with a reliable accuracy. As a low limit, can be considered a prediction of the MT_CKD-2.5 model [13] which is based on satellite measurements and is equal to 2.4×10^{-23} $\mathrm{cm^2\,mol^{-1}\,atm^{-1}}$ at 287 K for self-continuum, while upper estimates found in laboratory conditions [16] and [20] at similar temperatures are 3.6×10^{-23} (293 K) [16] and 3.4×10^{-23} $\mathrm{cm^2\,mol^{-1}\,atm^{-1}}$ (289 K) [20], respectively. The error of these measurements is rather high (up to 2.5×10^{-23}). Measurements [17], made with a lower error, but at higher temperatures, gave values of $(2.2 \pm 1) \times 10^{-23}$ (311 K), $(1.3 \pm 0.6) \times 10^{-23}$ (318 K), and $(0.8 \pm 0.3) \times 10^{-23}$ (325.5 K) $\mathrm{cm^2\,mol^{-1}\,atm^{-1}}$. Extrapolation of these results to $T = {\sim}290$ K gives a value no lower than 4.5×10^{-24} [17]. Finally, the analysis of aircraft measurements of the brightness temperature of downward radiation [27, Fig. 10], has shown that the self-contin-

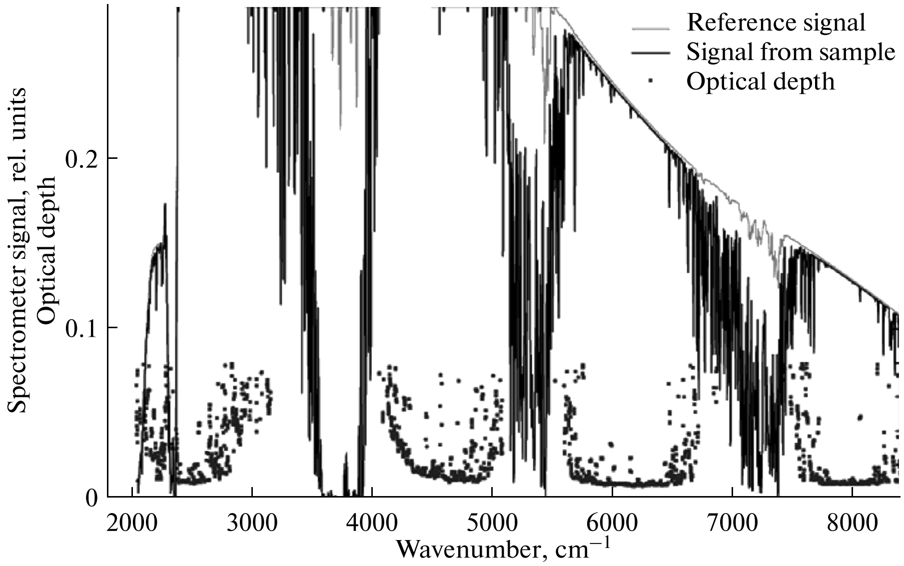

Fig. 3. Example of a "reference" spectrometer signal (from the empty cell), a signal from the cell filled with water vapor, and the optical depth retrieved. The reference signal was calibrated to be equal to the continuum optical depth of 0.01 in the 2500 cm^{-1} region. The water vapor pressure is 12.4 mbar, $T = 287$ K, a path length is 1065 m.

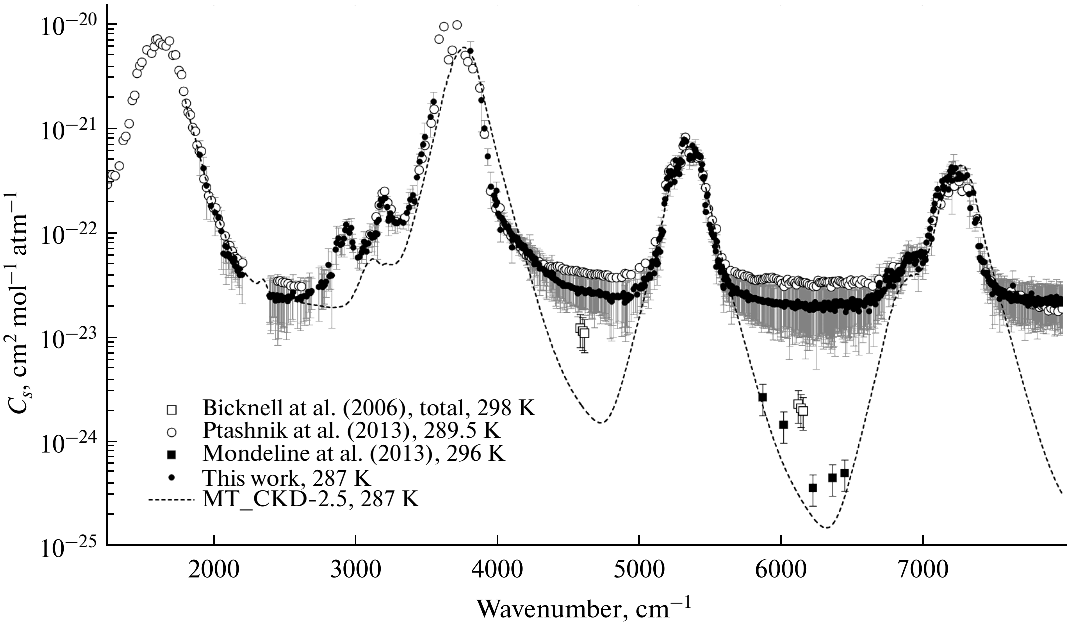

Fig. 4. Self-continuum absorption cross-section retrieved in this work at $T = 287$ K as compared to the results of previous measurements by Ptashnik et al. [20], Bicknell et al. [21], and Mondeline et al. [22]. The MT_CKD-2.5 continuum model [13] is shown by the dotted curve.

uum magnitude in this region should be approximately between the value found in [16] and that predicted by the MT_CKD-2.5 model [13].

We have decided to choose the quantity from the MT_CKD-2.5 model as a reference value of continum absorption in the 2500 cm^{-1} range, i.e., the lower estimation of the continuum. Consequently, $I_0(\nu)$ in Eq. (1) was multiplied by a constant, for the optical depth of the continuum in the 2500 cm^{-1} range was equal to 0.01, which at a path length of 1065 m and water vapor pressure of 12.4 mbar corresponds to the self-continuum absorption cross-section in the MT_CKD-2.5 model (Fig. 3).

RESULTS

The retrieved cross-section of the self-continuum absorption is shown in Fig. 4 in comparison with results of preceding measurements and the MT_CKD-2.5 continuum model [13]. On the whole, a good agreement between the new data and the results of similar preceding measurements is seen [20]. A lower continuum magnitude in the transparency windows in new measurements as compared to data [20] is caused by the fact that the former was calibrated to the MT_CKD-2.5 model in the 2500 cm^{-1} range.

The given measurements cannot pretend to a high accuracy in the determination of the absolute value of the continuum absorption. However, they give a sufficiently precise pattern (with an error of ~30–40%) about relative magnitudes of the continuum absorption in transparency windows of the region under study. The observations confirm conclusions of [20] that the absorption self-continuum in near-IR transparency windows changes from window to window much more weakly (by no more than 20–30%) than assumed by the MT_CKD-2.5 model [13].

CONCLUSIONS

A significant contradiction between the results of different measurements of the continuum absorption still persists at least in two near-IR atmospheric transparency windows: 4600 (2.1 μm) and 6300 cm^{-1} (1.6 μm) [16, 20–22]. Reasons for this contradiction can be the physically different measurement techniques and/or different influence of surface effects (for example, adsorption of water clusters of water on walls) when using cells of different sizes (from a half-meter [20] to several millimeters [22]). In order to solve this problem, further investigations are required.

The situation can be clarified, for example, with the help of measurements similar to [22], but in the 2500 cm^{-1} window (4 μm), where the magnitude of the continuum absorption is reasonably well known today from satellite and laboratory measurements. Any present-day measurements of the continuum absorption in the 2.1, 1.6, and 1.2 μm windows on paths longer than 2–3 km could be useful in order to provide higher values of the optical depth than is obtained in this work (0.01), and, correspondingly, a lower error. The principal problem of field measurements of the continuum on long paths is the correct exclusion of the aerosol component, which “masks” the water vapor continuum absorption.

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