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Determination of water vapor continuum absorption coefficient in 0.900 μm spectral range

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Photoacoustic measurements of water vapor absorption in mixture with nitrogen were carried out for the first time in the transparency micro-windows near 0.900 μm on the basis of cw Ti:Sapphire laser. The retrieved value of the water continuum absorption $(2.9 \pm 0.8) \cdot 10^{-25} \text{ cm}^2 \times \text{mol}^{-1} \cdot \text{atm}^{-1}$ exceeds the prediction of the CKD-2.4 and MT_CKD continuum models by 15 and 75%, respectively.

Despite more than half-century investigations, the problem of water vapor continuum absorption still attracts a considerable attention of theorists and experimenters. The nature of the phenomenon itself, as well as the magnitude of the continuum in an individual spectral regions remain open to question up to now. As is known, the most usable recent semiempirical continuum model CKD (Ref. 1), including its last versions CKD-2.4 (Ref. 2) and MT_CKD (Ref. 3), has been obtained through fitting to experimental data only in the far and mid-infrared spectral regions; and has no systematic verification in

the near-infrared and visible ranges. Moreover, individual experiments in this region⁴⁻⁶ demonstrate in some cases a significant disagreement with the CKD model, particularly, in spectral ranges, where a strong radiation absorption by water dimers is supposed.^{7,8}

This paper reports on determination of the water vapor continuum absorption near 0.900 μm (11100–11118 cm^{-1}) with the help of the spectrometer based on cw single-frequency ring Ti:Sapphire laser TIS-SF-07 (<http://www.tekhnoscan.ru>) and the photoacoustic resonance cell. The schematic plot of the spectrometer is presented in Fig. 1.

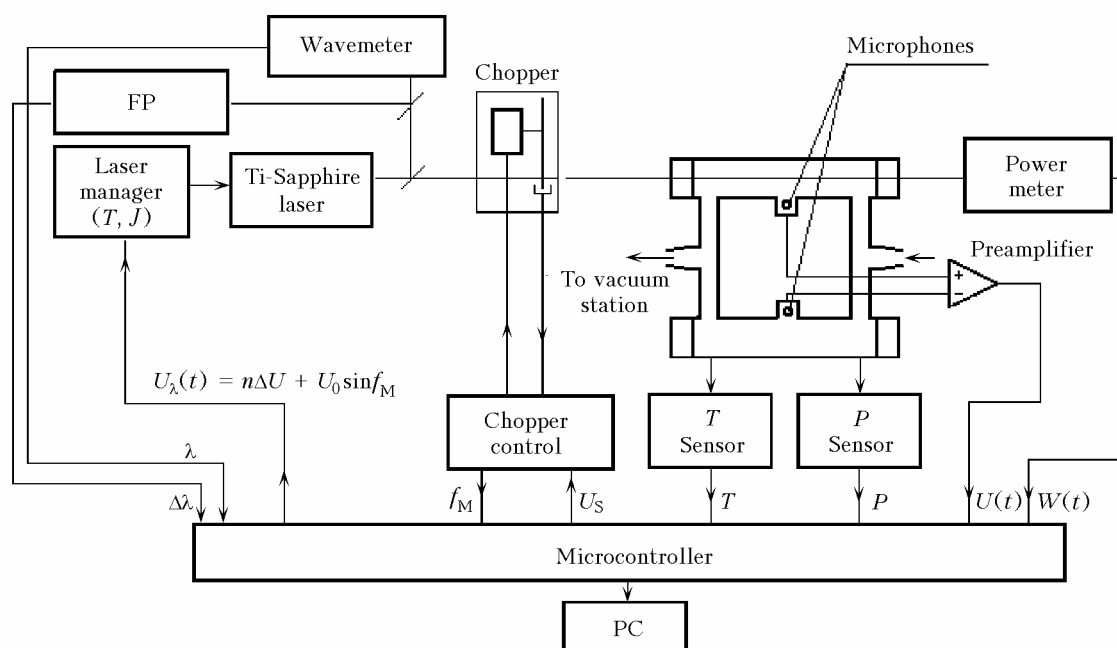


Fig. 1. Schematic plot of spectrometer with a resonance photoacoustic cell based on the cw tunable Ti:Sapphire laser.

The laser radiation power in 0.75–0.95 μm spectral range varies between 0.5 and 1 W depending on the generation wavelength. The radiation line width is less than 5 MHz (0.0002 cm^{-1}), i.e., much less than the characteristic half-width of the absorption spectral lines in air at pressures close to atmospheric. The range of smooth computer-controllable radiation frequency tuning is 10 GHz (0.33 cm^{-1}). The initial frequency tuning is manual throughout the range. The laser radiation frequency is controlled with the WS/5 wavelength meter (http://www.toptica.com/page/wavelength_meter_angstrom.php) at the error $\Delta\nu/\nu$ of 10^{-7} .

The photoacoustic resonance cell is a modification of the Helmholtz resonator, consisting of two identical cylindrical cells of 0.15 m in length and 0.006 m in diameter connected with each other by two capillaries. A Knowles-3027 microphone of $10\text{ mV}\cdot\text{Pa}^{-1}$ is mounted into the middle of the each cell. At a laser radiation power of 1 W the spectrometer threshold sensitivity for the absorption coefficient is $(4 \pm 2) \cdot 10^{-9}\text{ cm}^{-1}$. The measurement procedure is described in detail in Ref. 9.

Figure 2 presents an example of the absorption spectrum for a mixture of water vapor at a pressure of 20 mbar and nitrogen at a pressure of 1000 mbar.

The too small range of the laser smooth tuning, as well as unstable generation because of a high concentration of water vapor inside the laser cavity during the experiment (conducted in summer time) did not allow a sufficient measurement accuracy at other water vapor pressures.

The spectrometer was calibrated against the maximum of H_2O absorption line at 11116.7 cm^{-1} and the spectral part between two lines near 11107.3 cm^{-1} , i.e., all measured absorption values were multiplied by a scaling factor fitting the calculation and experiment in the given spectral

parts. Calculations were carried out based on the HITRAN-2004 database.¹⁰ Taking into account that intensities and broadening coefficients of the corresponding strong lines (11107.160 ; 11107.7097 and 11116.66 cm^{-1}) close to the interval under study are known with an error not exceeding 2–5 and 2%, respectively (according to error index in HITRAN-2004), there is a reason to believe that the calibration error does not exceed 5–7%.

Since the pure nitrogen was used as a buffer gas and the broadening coefficients in HITRAN are given for air, they were corrected in this work. Earlier (Refs. 11 and 12) it was shown that the ratio of the broadening coefficients for water vapor lines in air and nitrogen is about 0.9 within the given spectral range. Therefore, the broadening coefficients for air from HITRAN-2004, increased by 10%, were used in our calculations.

The continuum absorption within 11112.6 cm^{-1} was determined as a difference between the measured and calculated absorptions. In this case, in accordance with the CKD model formalism¹ only the local line contribution was taken into account in the calculations (i.e., taken within 25 cm^{-1} from each line center and decreased by the absorption value at the edge of the interval). The obtained result allows the estimation of the continuum absorption coefficient in the $0.900\text{ }\mu\text{m}$ spectral range at a level $(1.4 \pm 0.4) \cdot 10^{-7}\text{ cm}^{-1}$ at a water vapor pressure of 20 mbar, nitrogen pressure of 1000 mbar, and a temperature of 300 K (absorption cross section $(2.9 \pm 0.8) \cdot 10^{-25}\text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{atm}^{-1}$). Main contribution to the error is due to the inaccuracy of spectral line parameters in HITRAN-2004 (the contribution to the resulting error $\sim 0.2 \cdot 10^{-7}\text{ cm}^{-1}$), the error in determination of water vapor pressure in the cell $\sim 1\text{ mbar}$ (final contribution $\sim 0.07 \cdot 10^{-7}\text{ cm}^{-1}$), and random measurement error.

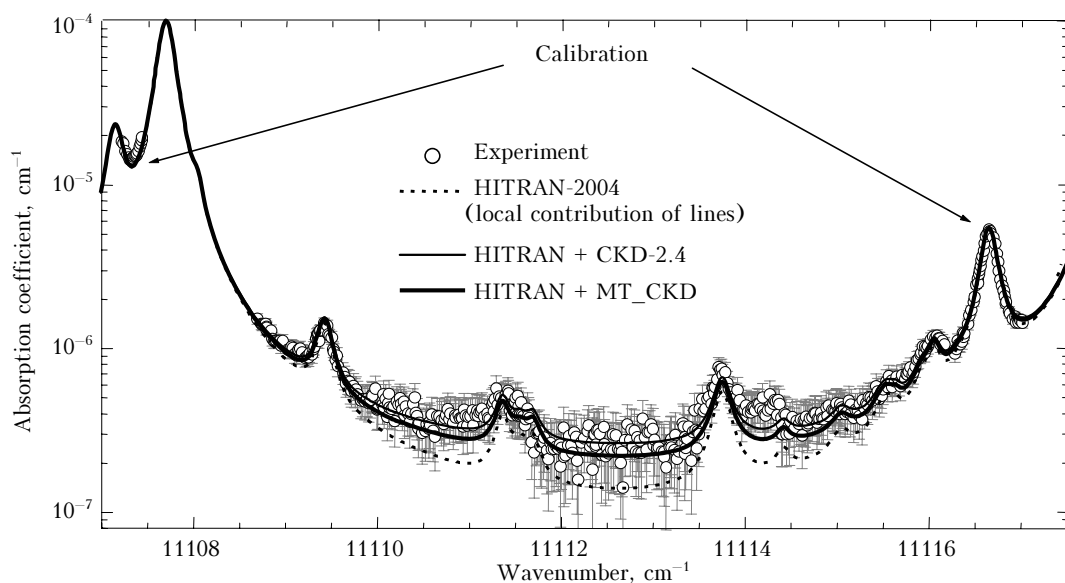


Fig. 2. Measured and calculated spectra of water vapor absorption coefficients for a mixture of 20 mbar H_2O + 1000 mbar N_2 at a temperature of 300 K.

Figure 2 shows that, as different from the result obtained, for example, for 0.694 μm region,⁶ the retrieved value of the continuum absorption in this case much better corresponds to the CKD-2.4 continuum model, than to the MT_CKD version ($1.24 \cdot 10^{-7}$ and $0.80 \cdot 10^{-7} \text{ cm}^{-1}$, respectively, under the experimental conditions), exceeding the model predictions by 15 and 75%, respectively.

In future, of interest in this spectral range can be measurements in a pure water vapor because of possible essential contribution of water dimers into the self-broadening continuum.

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