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# Study of $H_2O$ line broadening and shifting by $N_2$ pressure in the 16,600–17,060 $cm^{-1}$ region using FT-spectrometer with LED source

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ABSTRACT

$N_2$ pressure broadening and shifting coefficients are presented for about 300 strongest water vapor lines in the 16,600–17,060 $cm^{-1}$ spectral region. The spectra have been recorded with a spectral resolution of 0.05 $cm^{-1}$ at room temperature by a Fourier transform spectrometer using a high luminance LED light source. A high signal-to-noise ratio (S/N ≈ 10 000) permits the analyses of the lines with intensities from $1.54 \times 10^{-23}$ to $2.0 \times 10^{-26}$ cm/molecule. The multi-spectrum fitting procedure was used to fit line parameters of the $\nu_1+4\nu_2+2\nu_3$, $3\nu_1+2\nu_2+\nu_3$, $4\nu_1+\nu_3$, $4\nu_1+2\nu_2$, $5\nu_1$ bands for the temperature $T=297$ K. Line broadening and shifting calculations are performed using a semi-empirical method, which is based on the impact theory of broadening, and includes the correction factors whose parameters were determined by fitting the broadening coefficients of 12 lines to the experimental data. The method was further developed for the estimate of line profiles using the an harmonic wave functions.



## 1. Introduction

The coefficients of the water vapor line broadening induced by the pressure of $N_2$, $O_2$, $H_2O$ are of interest to many atmospheric applications. For example, $H_2O$ absorption line parameters are needed for the determination of narrow-band optical radiation energy losses along vertical inhomogeneous paths. The need for reliable line profiles has motivated a large number of the line parameter measurements in a wide spectral range - from the microwave to visible and near UV regions (see, for example, [1] and references therein) but only 3 papers are devoted to the line profile parameter measurements in the considered region between 16,600 and 17,060 $cm^{-1}$ [2–4].

In the visible range, line intensities are very small ($10^{-25}$–$10^{-28}$ cm/mol) and in order to investigate their profile, one has to use a spectrometer with a threshold sensitivity as high as $10^{-6}$–$10^{-8}$ $cm^{-1}$. To achieve this high sensitivity, Fourier transform spectrometers employ long multipass absorption cells with a base length exceeding 4 m, as, for example, the spectrometers in Reims and Tomsk with, respectively, 50 and 30 m bases [5,6]. Large dimensions of such cells impair their thermal stabilization properties required for long-time measurement and make it difficult to achieve a high signal-to-noise ratio and to get accurate data on line broadening. Earlier [7,8], we suggested using Light Emitted Diodes (LEDs) with high radiation intensity as an emitter in the high resolution Fourier spectrometer with multipass cells and showed that one can achieve the detection sensitivity comparable to the laser equipment.

In the high frequency region, where the spectra have a low signal-to-noise ratio, the correlations between some lineshape parameters make data fitting difficult. In such cases the multi-spectrum fitting approach allowed to overcome this problem [9]. In the multi-spectrum fitting method, the line parameters are fitted to a set of spectra measured at different gas pressures. This approach makes it possible to measure the pressure-dependence of the collision-induced line-width component and to obtain the line parameters consistent in a wide range of gas pressures.

Some effects of the vibrational-rotational dynamics related to the chaotic behavior under strong excitation in water vapor spectra were considered by the authors in Ref. [11]. They are an anomalous centrifugal distortion, HEL-resonances in $H_2O$, the vibrational dependence of the line contour parameters, and the effect of intramolecular resonances on interference lines. Here we use the approach which takes into account the vibrational dependence and

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**Table 1**
Summary of experimental conditions of the $H_2O$ spectra.

| Sample number | $H_2O$ pressure, mBar | $N_2$ pressure, mBar | Temperature, K |
|---|---|---|---|
| 1 | 16.5 | 0 | 297 |
| 2 | 16.5 | 128.3 | 297 |
| 3 | 16.5 | 400.1 | 297 |
| 4 | 16.5 | 987 | 297 |

intramolecular resonances automatically. Line parameter were calculated using the semi-empirical method [12], which includes the correction factors whose parameters can be determined by fitting the broadening coefficients to the experimental data. This approach combined with the method of effective Hamiltonians was applied to calculate the line profile parameters and their temperature dependence for the $H_2O$ molecule broadened by different buffer gases [13–17]. The method was further improved using the exact vibration-rotation wave functions calculated by the variational method. This approach takes into account the contributions of all scattering channels induced by molecular collisions. We used this method to obtain collisional broadening and shifting coefficients of $H_2O$ lines in a wide spectral range for the $H_2O$-air colliding system [18,19].

The paper is organized as follows. The details of experimental procedure are given in the next section. Section 3 contains a description of the theoretical foundations and presents certain details of line profile calculations. In Section 4, we present the results and compare them with the data available in literature.

## 2. Experiment

The absorption spectra of the $H_2O$-$N_2$ species between 16,600 and 17,060 $cm^{-1}$ were recorded using IFS-125M Fourier transform spectrometer with the boxcar apparatus function and a spectral resolution of 0.05 $cm^{-1}$. A cell with a base length of 60 cm and a multipass White optical scheme was used with an optical path length of 24 m. The measurements were performed in a temperature-stabilized room at a fixed temperature of $297 \pm 1$ K. The small length of the cell makes it easier to maintain a stable temperature over the entire optical path. As a radiation source, we used a CREE XPE AMB light-emitting diode with a high spectral brightness in the region of 0.59 μm (with a maximum in the spectral range 16,700–16,900 $cm^{-1}$). The high spectral brightness of the LED, exceeding by two orders of magnitude the brightness of halogen lamps in this spectral region, provides a sufficiently high signal to noise ratio (S/N) to record weak absorption. It allowed us to obtain a signal-to-noise ratio of about 10,000 and to detect weak absorption lines with intensities on the order of $10^{-26}$ cm/mol. The measurements were performed over several days; each spectrum was obtained by averaging over 3456 scans. The technique that uses light-emitting diodes is described in more details in Refs. [8,9].

In this study, the absorption spectra of four samples were recorded: $H_2O$ pressure was 16.5 mbar, $N_2$-pressure varied from 128 to 987 mbar. The pressure measurements were performed by a pressure transducer AIR-20M with the pressure measurable range 0–100 kPa and an accuracy of the order of 0.1%. The pressure was additionally checked using intensity of the lines of the absorber ($H_2O$). The measurement conditions are shown in Table 1.

Fig. 1 shows a part of the $H_2O$ transmission spectrum measured in the range under study. Note that the minimal transmission in this spectral range is T = 0.980. The noise in the spectrum is less 0.01% that allows the studies of line broadening with high accuracy using the multi-spectrum fitting procedure.

The line parameters were determined with the Wxspe software package, which is able to perform an automatic search of peaks

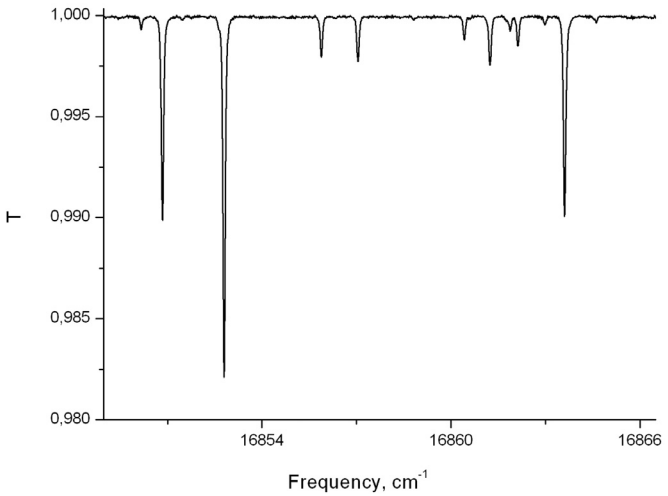


**Fig. 1.** $H_2O$–$N_2$ transmission spectrum in the region 16,850–16,866 $cm^{-1}$.

using methods of pattern recognition theory [20]. This software package not only finds the peaks in the spectrum, but can also perform least-squares fits of the contour parameters to the measured dataset using the Tikhonov regularization procedure. The multi-spectrum fitting technique allows to fit simultaneously a number of spectra (four in our case) over a chosen wave number interval involving 1–3 lines. For groups of overlapping lines, the parameters of all lines were fitted simultaneously. In the multi-spectrum fitting technique it is possible to retrieve simultaneously values for all the line parameters including line positions and intensities, values of pressure-broadening coefficients and pressure-induced shift coefficients. The program has several built-in types of contours - the contours of Lorentz, Doppler, Voigt, Speed-dependent Voigt, and the Hartman-Tran profile (HTP) [10]. Details of the analysis procedure are given in our previous work [20]. In the fitting algorithm, the experimental spectra and synthetic spectra are matched by minimizing the sum of the squares of the residuals between the experimental and calculated spectra. This was achieved by adjusting the values of various line parameters mentioned above, as well as the parameters of the spectrometer real apparatus function.

Recently, various line shape models, which take into account velocity-changing collisions, have been widely tested. Lisak et al. [9] have analyzed various semiclassical line-shape models, which include the influence of the Dicke narrowing and the speed dependence of pressure broadening for the case of $H_2O$ in the region of 10,600 $cm^{-1}$. It has been found that the line contour parameters (intensity and broadening factor) are underestimated by 4–6% when using the Voigt contour to describe the experimental data.

We compared using the contours of Hartman-Tran and Voigt in the analysis of several strong $H_2O$ lines. At low pressure ($P(H_2O) = 16.5$ mBar, $P(N2) = 0$) the fit residuals between the experimental data and the Voigt profile give the w-shaped structure, which disappears when processing by the Hartman-Tran profile (RMS of the fit is reduced by 2.5 times). The differences between the halfwidths determined from the Voigt and the Hartman-Tran profiles are 6–10%. At higher pressures, this difference decreases and tends to zero at a buffer gas pressure of 300 mbar, when the differences in intensities and line widths do not exceed 0.1%. In the multi-spectrum fitting, the difference between the broadening factors determined from these contours does not exceed 0.2%. Neither the resolution nor the signal-to-noise ratios in our spectra were sufficient to determine the speed dependence parameters for the observed transition.

The multi-spectrum fitting method minimizes the random errors that may arise due to the spectrum noise level. In order to