

SPECTROSCOPY OF ATOMS
AND MOLECULES

LED-Based Fourier Transform Spectroscopy of H₂¹⁶O
in the Range 15500–16000 cm⁻¹

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Abstract—The vibrational–rotational absorption spectrum of water vapor within the range 15500–16000 cm⁻¹ is measured and analyzed. The spectrum is recorded with an IFS-125M Fourier transform spectrometer with a resolution of 0.03 cm⁻¹, at pressure of 25 mbar, at a temperature of 24°C, and at an optical path length of 34.8 m. The measurements are performed using a multipass White cell with a base length of 60 cm. A light-emitting diode is used as a radiation source. The signal-to-noise ratio is about 10⁴, which makes it possible to measure the parameters of lines with intensities on the order of 10⁻²⁷ cm/molecule. The centers, intensities, and half-widths of lines are determined by fitting the Voigt profile parameters to measured data set by the least squares method. A list of more than 430 lines is formed based on the analysis of the spectrum. The obtained results are compared with calculated and experimental data of other authors.

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INTRODUCTION

Investigations of the absorption, emission, or scattering spectra of water vapor in a wide spectral range (from microwave to visible) are of interest for atmospheric optics and atmospheric chemistry, problems of remote sensing of atmospheric gases, production of super-pure materials, and many other scientific and technical problems. Therefore, the high-resolution spectra of H₂O molecules have been the subject of multiple studies. Spectroscopic information obtained by measurements is subjected to complete and careful analysis, which includes determination of the spectroscopic parameters of lines (centers, intensities, broadening and shift coefficients, and their temperature dependence coefficients) and their vibrational–rotational assignments. Precise measured spectral information is contained in spectroscopic databases, such as e.g., HITRAN, GEISA, W@DIS, and SPECTRA.

In the present work, we measure and analyze the absorption spectrum of water vapor with a natural content of water isotopes in the region of 0.625 μm. The range under study includes transitions to highly excited vibrational–rotational states, which belong to the (311)–(000), (113)–(000) bands, and other bands coupled to them by accidental resonances [1]. The absorption lines are rather weak: their intensities are less than 10⁻²⁴ cm/molecule. To measure such spectra, it is necessary to use highly sensitive measurement methods.

The absorption spectra of water vapor in the visible region have been repeatedly studied before (see, for example, [2–7] and references therein). Note also that, to date, the centers and intensities of the spectral lines of H₂¹⁶O are precisely calculated in the entire optical region [8, 9], including the range studied in this work. At the same time, it is necessary to systematically verify both the measurement results and the theoretical calculations.

Previously [10], we showed that a high sensitivity in measurements of weak absorption spectra can be achieved by using high-power light-emitting diodes, which ensure a high signal-to-noise ratio. In the present work, we use a CREE XPERED diode, emitting in the range 15500–16000 cm⁻¹ with a high spectral brightness, which allows one to perform highly sensitive measurements at a small optical path length.

The aim of this work is to record and analyze the absorption spectrum of water vapor in the spectral range 15500–16000 cm⁻¹ using the above-mentioned technique, as well as to refine and verify the parameters of H₂¹⁶O spectral lines.

MEASUREMENTS AND DATA PROCESSING

The experimental absorption spectrum of H₂¹⁶O in the range 15500–16000 cm⁻¹ was recorded using an IFS-125M Fourier transform spectrometer with a resolution of 0.03 cm⁻¹ at a pressure of 25 mbar and an

Table 1. Centers and intensities of strong lines (with intensities exceeding 9×10^{-26} cm/molecule) determined in our study and in [3, 8, 9]

Line center, cm ⁻¹ (our study)	Intensity, cm/molecule (our study)	Line center, cm ⁻¹ [8]	Intensity, cm/molecule [9]	Line center, cm ⁻¹ [3]	Intensity, cm/molecule [3]
15536.7869	1.47E-25	15536.7878	1.56E-25	15536.7885	1.57E-25
15540.6584	2.01E-25	15540.6624	2.19E-25	15540.6617	2.19E-25
15560.0941	1.48E-25	15560.0975	1.64E-25	15560.0968	1.63E-25
*15579.3640	9.87E-26	15579.3492	3.59E-26	15579.3631	4.83E-26
		15579.3864	2.98E-26	15579.3631	4.18E-26
*15690.4187	1.21E-25	15690.4216	1.38E-25	15690.4203	1.66E-25
		15690.4129	0.16E-25	15690.4203	4.73E-26
15691.1692	1.21E-25	15691.1685	1.14E-25	15691.1706	1.23E-25
15698.0775	1.64E-25	15698.0789	1.62E-25	15698.0797	1.75E-25
15715.8739	2.44E-25	15715.8757	2.16E-25	15715.8763	2.38E-25
15730.5596	1.29E-25	15730.5606	1.24E-25	15730.5613	1.32E-25
15739.7722	9.95E-26	15739.7725	1.03E-25	15739.7749	1.11E-25
15741.9222	2.75E-25	15741.9226	2.67E-25	15741.9236	2.95E-25
15750.3832	1.49E-25	15750.3832	1.46E-25	15750.3847	1.61E-25
15751.1145	2.86E-25	15751.1159	2.84E-25	15751.1161	3.13E-25
15762.5568	3.50E-25	15762.5585	3.50E-25	15762.5583	3.91E-25
15765.3944	1.05E-25	15765.3944	1.01E-25	15765.3957	1.11E-25
15785.3835	1.18E-25	15785.3841	1.12E-25	15785.3843	1.29E-25
15788.2767	2.45E-25	15788.2774	2.39E-25	15788.2781	2.66E-25
*15808.6367	1.76E-25	15808.6208	0.90E-25	15808.6294	1.28E-25
15808.7693	1.44E-25	15808.7695	1.36E-25	15808.7702	1.26E-25
15808.9705	2.29E-25	15808.9710	2.17E-25	15808.9713	2.37E-25
15815.0938	1.56E-25	15815.0925	1.34E-25	15815.0946	1.49E-25
15818.5537	2.80E-25	15818.5542	2.86E-25	15818.5549	3.15E-25
*15818.7664	1.03E-25	15818.7665	1.21E-25	15818.7669	1.35E-25
15819.0277	9.27E-26	15819.0315	9.71E-26	15819.0295	1.06E-25
15824.8474	1.34E-25	15824.8475	1.31E-25	15824.8476	1.5E-25
15825.4021	3.06E-25	15825.4021	3.02E-25	15825.4031	3.36E-25
15827.6375	4.00E-25	15827.6379	3.89E-25	15827.6387	4.35E-25
15836.2644	1.02E-25	15836.2645	0.97E-25	15836.2648	1.09E-25
15844.9843	1.23E-25	15844.9854	1.21E-25	15844.9853	1.36E-25
15870.5374	1.09E-25	15870.5358	1.06E-25	15870.5369	1.19E-25
15875.5263	4.36E-25	15875.5258	4.28E-25	15875.5266	4.79E-25
15882.1108	2.93E-25	15882.1100	2.90E-25	15882.1108	3.25E-25
15887.2653	4.67E-25	15887.2645	4.64E-25	15887.2653	5.14E-25
15891.7374	1.75E-25	15891.7345	1.69E-25	15891.7372	1.88E-25
15896.0216	2.28E-25	15896.0212	2.18E-25	15896.0216	2.46E-25
15899.0464	1.21E-25	15899.0462	1.05E-25	15899.0485	1.13E-25
15904.4626	5.03E-25	15904.4619	4.97E-25	15904.4628	5.49E-25
15904.6216	1.50E-25	15904.6226	1.30E-25	15904.6234	1.44E-25
15912.8372	4.12E-25	15912.8356	4.08E-25	15912.8369	4.41E-25
15915.0585	1.43E-25	15915.0567	1.41E-25	15915.0578	1.52E-25

Table 1. (Contd.)

Line center, cm^{-1} (our study)	Intensity, $\text{cm}/\text{molecule}$ (our study)	Line center, cm^{-1} [8]	Intensity, $\text{cm}/\text{molecule}$ [9]	Line center, cm^{-1} [3]	Intensity, $\text{cm}/\text{molecule}$ [3]
15923.3815	1.05E-25	15923.3823	1.04E-25	15923.3837	9.67E-26
15923.9929	1.23E-25	15923.9909	1.18E-25	15923.9924	1.3E-25
15924.1718	3.68E-25	15924.1706	3.76E-25	15924.173	3.81E-25
15924.3075	3.37E-25	15924.3077	3.19E-25	15924.3078	3.52E-25
15925.5245	2.61E-25	15925.5228	2.51E-25	15925.5244	2.8E-25
15931.1563	2.15E-25	15931.1564	1.93E-25	15931.1566	2.05E-25
15938.3132	1.14E-25	15938.3130	1.20E-25	15938.3137	1.26E-25
*15938.5462	1.50E-25	15938.5455	1.05E-25	15938.5462	4.75E-26
		15938.5443	0.41E-25	15938.5462	1.17E-25
15939.6454	9.65E-26	15939.6480	9.48E-26	15939.6486	1.02E-25
*15943.9498	1.32E-25	15943.9397	2.11E-26	15943.9441	2.04E-26
		15943.9414	6.65E-26	15943.9441	8.26E-26
15950.6662	1.88E-25	15950.6661	1.84E-25	15950.6661	2.0E-25
15967.3406	1.37E-25	15967.3384	1.32E-25	15967.3401	1.42E-25

* Doublet lines and lines near strong ones.

optical path length of 34.8 m. A cell with a base length of 60 cm and a multipass White optical scheme were used. The measurements were performed in a temperature-stabilized room at a fixed temperature of $24 \pm 1^\circ\text{C}$. The small length of the cell makes it easier to keep a stable temperature over the entire optical path. As a radiation source, we used a Cree XPERED light-emitting diode with a high spectral brightness in the region of $0.625 \mu\text{m}$ (with a maximum in the

$15670\text{--}15870 \text{ cm}^{-1}$ spectral range), which allowed us to obtain a signal-to-noise ratio of about 10^4 and to detect weak absorption lines with intensities on the order of $10^{-27} \text{ cm}/\text{molecule}$. To achieve a high signal-to-noise ratio, the measurements were performed over several days and the spectrum was obtained by averaging over 17136 scans. The measurement technique with the use of light-emitting diodes is described in more detail in [10–12].

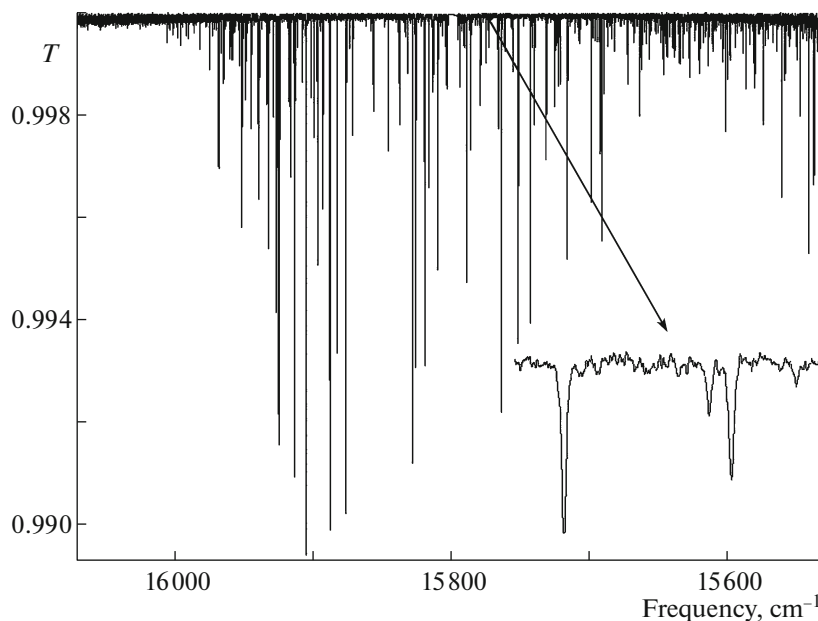


Fig. 1. Experimental transmission spectrum of H_2^{16}O in the range $15500\text{--}16000 \text{ cm}^{-1}$.

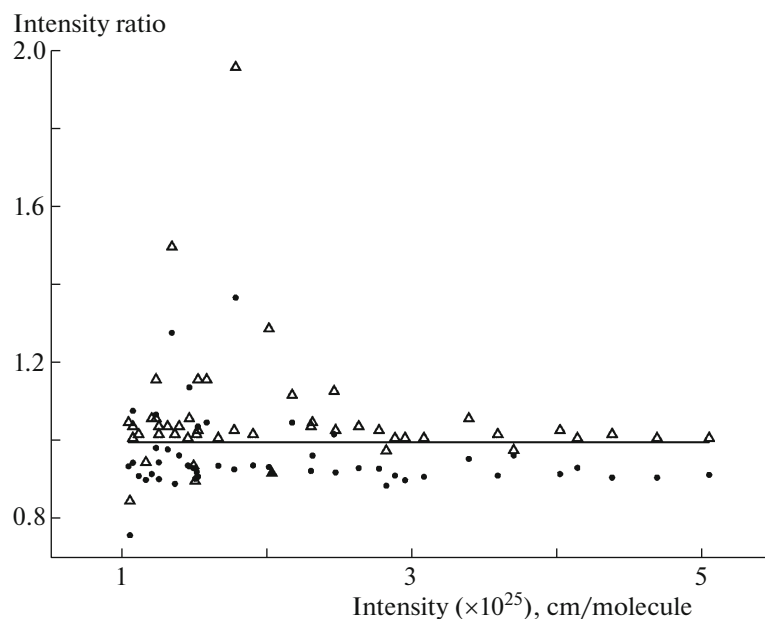


Fig. 2. Comparison of the intensities of the strongest lines (with intensities exceeding 9×10^{-26} cm/molecule): Δ is the ratio of our data to the calculated values from [9], and \bullet is the ratio of our data to the measured intensities from [3].

Figure 1 shows a transmission spectrum measured in the range under study. Note that the minimal transmission is $T = 0.990$; the inset shows the spectrum in a narrow range containing only very weak lines with transmission on the order of $T = 0.9997$. The radiation of a He–Ne laser used in the measuring system of the spectrometer falls into the range 15794.8 – 15801.3 cm^{-1} , because of which this range was cut out of the total spectrum.

The obtained spectral data were calibrated using the centers of lines calculated in [8]. Actually, the data of the International Union of Pure and Applied Chemistry (IUPAC) project [8] were used in our work as secondary frequency standards, since the energy levels and the centers of the H_2^{16}O lines presented there are most precise to date.

The line parameters were determined with using a Wxspe software package, which uses pattern recognition methods [13]. This package allows one not only to find the line peaks, but also to fit the contour parameters (Voigt contour in our case) by the least squares method to the measured data set. For each parameter of the contour, its center, halfwidth, and intensity, we determined confidential intervals. For groups of overlapping lines, the parameters of all lines were fitted simultaneously. Fitting was performed taking into account the triangular instrumental function with a width of 0.03 cm^{-1} . For some lines, for which the noise level was comparable with the signal, the centers and intensities were determined from absorption line peak. Intensities were analyzed using, as additional data for comparison and control, the line intensities calculated in [9] with a highly accurate ab initio dipole moment

function. The analysis of the spectra in the range considered revealed 434 lines with intensities from 2×10^{-27} to 5×10^{-25} cm/molecule.

RESULTS AND DISCUSSION

Table 1 lists the centers and intensities of strongest lines in the range from 15536 to 15698 cm^{-1} (the intensities of which exceed 9×10^{-26} cm/molecule) obtained in our work in comparison with the experimental data of work [3, 8, 9]. The determination of spectroscopic parameters of lines with lower intensities is problematic due to a low signal-to noise ratio, because of which the parameters are determined with large errors. More complete data, including weak lines and quantum numbers of transitions, are presented in spectroscopic databases [14–17].

The calculated spectra of the H_2^{16}O molecule are given in [8, 9]. The centers of lines in [8] were determined as a result of an appropriate theoretical treatment, so that the data presented are the best at the moment. The line list from [8] were added by the intensities of lines from [9], which were calculated with highly accurate vibrational–rotational wave functions and an ab initio dipole moment function of H_2^{16}O [18]. The typical error of these calculated intensities for strong lines is 5–10%.

Figure 2 shows the ratio of the intensities of the strongest lines (with intensities exceeding 9×10^{-26} cm/molecule) measured in our work to the calculated intensities from [9], as well as to the experimental intensities from [3]. As is seen from Fig. 3, our

Table 2. Centers and intensities of new H₂¹⁶O lines recorded in this work and data of [8, 9]

Line center, cm ⁻¹ (our study)	Intensity, cm/molecule (our study)	Line center, cm ⁻¹ [8]	Intensity, cm/molecule [9]	Upper state V ₁ V ₂ V ₃ J K _a K _c	Lower state V ₁ V ₂ V ₃ J K _a K _c
15751.4107	4.15E-27	15751.4107	8.74E-27	0 3 3 6 4 2	0 0 0 5 4 1
15764.7160	3.04E-27	15764.7286	1.68E-27	2 3 1 8 6 2	0 0 0 7 4 3
15777.6087	4.52E-27	15777.5938	4.07E-27	2 1 2 6 2 4	0 0 0 6 1 5
15813.0753	2.80E-27	15813.0802	2.69E-27	2 1 2 7 4 4	0 0 0 7 3 5

Intensities of lines in Table 2 are determined from the absorption in their peaks.

intensities on average agree rather well with the results of ab initio calculations in [9]. The ratio of the intensities obtained in our work to the intensities measured in [3] is systematically lower than unity, which testifies that the line intensities in [3] are obviously somewhat overestimated. The average ratio of our intensities of the strongest lines to the intensities calculated in [9] is 1.03 ± 0.07 , while the average ratio of the intensities from [3] to the calculated intensities from [9] is 1.09 ± 0.06 . Thus, we can conclude that our measured data agree with the data of work [3] within the measurement error and confirm the ab initio calculations of [9].

As is seen from Fig. 2, considerable deviations from the calculated data are observed for three lines centered at 15808.63 cm^{-1} (ratio $r = 1.96$), 15943.95 cm^{-1} ($r = 1.5$), and 15579.36 cm^{-1} ($r = 1.29$). The line centered at 15808.63 cm^{-1} is a doublet consisting of two closely spaced strong lines (the distance between their centers is 0.05 cm^{-1}). The line at 15943.95 cm^{-1} is a triplet with the components at $15943.939 \text{ cm}^{-1}$ (intensity $2.1 \times 10^{-26} \text{ cm/molecule}$), $15943.941 \text{ cm}^{-1}$

($6.6 \times 10^{-26} \text{ cm/molecule}$), and $15944.02375 \text{ cm}^{-1}$ ($2.2 \times 10^{-25} \text{ cm/molecule}$). The line centered at 15579.36 cm^{-1} also corresponds to two lines the calculated parameters of which are $15579.349 \text{ cm}^{-1}$ ($3.59 \times 10^{-26} \text{ cm/molecule}$) and $15579.386 \text{ cm}^{-1}$ ($2.98 \times 10^{-26} \text{ cm/molecule}$). From the data presented in Table 1, one can see that our data for the above-mentioned multiplets agree with the experimental data of [3] better than with the calculated intensities from [9].

The centers of lines measured in this work were compared with the experimental data of [3]. In [3], the spectra were recorded using a Fourier transform spectrometer with a resolution of $0.03\text{--}0.06 \text{ cm}^{-1}$ at a temperature of $292 \pm 3 \text{ K}$, a pressure of $6\text{--}18 \text{ hPa}$, an optical path length of 600 m (which allowed the authors to achieve the desired threshold sensitivity), and a signal-to-noise ratio of about 2500. It is necessary to note that the accuracy of determination of the centers of lines in our spectrum was affected by the pressure-induced shift. Since the greatest measured pressure-induced shift coefficient is, according to [19], $0.07 \text{ cm}^{-1} \text{ atm}^{-1}$, the error of determination of the line center corresponding to the pressure of 25 mbar may amount to 0.002 cm^{-1} . Figure 3 presents the statistics of deviations of line centers determined by us from the data of [3]. One can see that the difference in the centers does not exceed 0.04 cm^{-1} . The root-mean-square deviation of the centers of strong lines from calculated is 0.0014 cm^{-1} and 0.0007 cm^{-1} for our data and experimental results of [3], respectively, which lies within the experimental error. For 68% of lines, the difference between the centers does not exceed 0.006 cm^{-1} .

Table 2 presents the centers and intensities of lines that were found in our spectrum but are absent in the line list in [3]. The centers and intensities of these lines determined by us satisfactorily agree with the calculated data of [8, 9]. The data obtained can be considered as new results supplementing the measurements performed previously.

CONCLUSIONS

The use of light-emitting diodes as radiation sources made it possible to measure the centers and

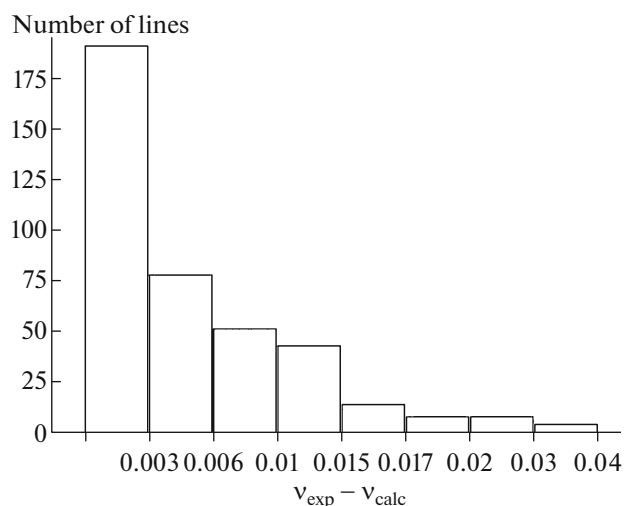


Fig. 3. Comparison of the centers of experimental lines determined in our study with the calculated data of IUPAC [8].

intensities of weak spectral lines of water vapor in the visible region in relatively short cells. The centers and intensities of lines determined by analyzing the spectra in general agree well with the experimental data of [3] and with the precise calculated data of [8, 9]. The intensities of strongest H_2^{16}O spectral lines measured in this work within the range studied agree with the results of previous measurements [3] within the measurement error, but are systematically 3% lower. At the same time, our data are closer to the results of ab initio calculations.

The results of this work show that the described method using light-emitting diodes as radiation sources makes it possible to record spectral lines with a high sensitivity at a considerably shorter optical path. The spectral data obtained in this work are included into the W@DIS information system [16] and can be used to refine the available data on water vapor absorption in the range 15 500–16 000 cm^{-1} .

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