

MEASUREMENTS OF THE TEMPERATURE BEHAVIOR OF THE H₂O–VAPOR SPECTRAL LINE SHIFTS AND BROADENING WITH A PHOTOACOUSTIC SPECTROMETER

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A modified dual-channel photoacoustic spectrometer with a pulsed ruby laser intended for studies of the spectral line contour temperature and pressure behavior is described. Some test measurements as well as measurements of the temperature behavior of the width and shift of the H₂O–vapor absorption line at 694.38 nm are conducted, this line being used as a reference one in lidar sensing of water vapor in the atmosphere.

Quantitative data on spectral line parameters of molecules, such as half-width and pressure shifts of line centers as well as their temperature-dependent variations are necessary for further development of spectroscopic techniques for sounding the atmospheric gas components and for calculating the energy attenuation of a narrow-band laser radiation along inhomogeneous atmospheric paths.^{1,2} The same data are of interest to studying physics of molecular collisions and determining the potential parameters of intermolecular interaction.³

Dual-channel photoacoustic (PA) spectrometers with tunable lasers serve as efficient instruments for measuring the parameters of weak spectral line contours, for example, H₂O absorption line within the visible spectral range, which are used as reference ones at sounding of atmospheric water vapor along vertical paths.^{4,5} Small size of PA cells allows one to relatively easily vary and control the temperature and pressure of a gas under study. As a consequence, the PA spectrometers find a wide use in investigation of widths and shifts of the molecular absorption lines by pressure of foreign gases including air.^{3–7}

In this paper we present a description of modification of a dual-channel PA spectrometer with a frequency-tunable pulsed ruby laser intended for measuring the temperature dependence of widths and shifts of H₂O absorption lines. Some results of corresponding measurements of the parameters of H₂O absorption lines broadened by air are also discussed.

The dual-channel PA spectrometer intended for measuring the shape and parameters of H₂O absorption line contours in the visible spectral range has been described in details in Refs. 5 and 7. Its spectral resolution is better than 0.015 cm⁻¹ within the ruby laser frequency tuning range (14397...14405 cm⁻¹) and the threshold sensitivity to the absorption coefficient is at the level of 5 · 10⁻⁸ cm⁻¹. The experiments on the H₂O absorption line self-shifting⁷ have shown its capability of reliably recording of an individual absorption line shift at the shift magnitude ≥ 0.003 cm⁻¹.

We have used two PA cells in the PA spectrometer placed successively along a laser beam. The first cell was used as a reference one. It was filled with a pure water vapor at a pressure of several Torr. The second cell was

used to measure the absorption line contour of H₂O, mixed with a buffer gas at different pressures within the temperature range from 290 to 400 K. Let us examine in more detail the construction of the second (thermal) cell and methods for measuring the temperature dependence of a spectral line width and shift.

CONSTRUCTION AND SPECIFICATIONS OF THE THERMAL PA CELL

The main difficulties of the thermal PA cell design are caused by the fact that the characteristics of a thin diaphragm of a highly sensitive microphone sensor (a capacitor microphone in our case) critically depend on the temperature.

Two types of PA cell are used for studies in different ranges of the working temperature:

1) the microphone sensor is in a thermal contact with a medium and thus its temperature coincides with the medium temperature;

2) the microphone sensor is thermally insulated from a media and its temperature is maintained at a preset level.

Analysis of both PA cells operation peculiarities has shown the first cell modification to be more advantageous when investigating the temperature behaviour of weak absorption spectra (the absorption coefficient ≤ 10⁻⁴ cm⁻¹) within a narrow temperature range. Just this modification was used in our experiments. Block diagram of the thermal PA cell is depicted in Fig. 1.

The PA cell 2, fully identical to the reference one, is placed into a thermostat 1. Inside the thermostat there are heating elements and a thermocouple for temperature control. To provide a stable operation of the microphone at a temperature rise, its diaphragm is made of a 10 μm-thick aluminium film. The diaphragm tension is chosen so that the maximum of the microphone sensitivity could be achieved in the middle of the working temperature range, i.e., at 340–350 K. In a fully dismountable construction of the microphone we used gaskets of Teflon. When assembling the unit we did not use any glue in order to avoid emission of foreign substances into the gas mixture under study at heating. The cell windows are also sealed with the Teflon gaskets. A signal from the capacitor microphone is directed to the microphone amplifier outside the thermostat. The accuracy of temperature stabilization inside the thermostat is ± 0.4 K.

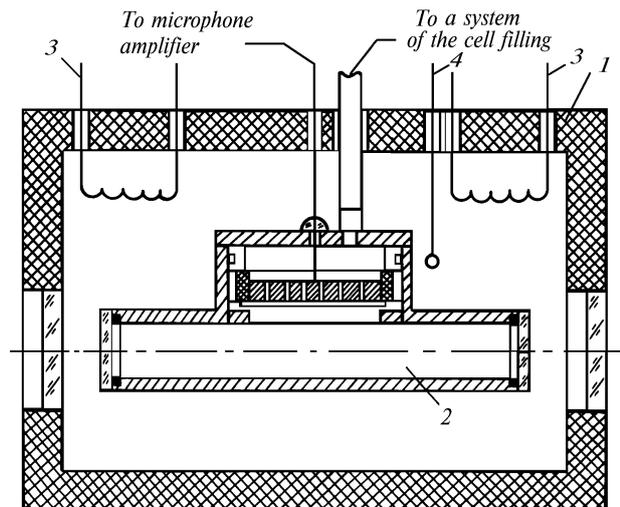


FIG. 1. Block diagram of the thermal PA cell: 1) thermostat, 2) PA cell, 3) heating elements, and 4) thermocouple.

The main specifications of the thermal PA cell are given below.

Range of temperature variation	290 ... 400 K
Stability of the temperature maintenance	± 0.4 K
Range of gas pressure variation in the cell	0.1 ... 760 Torr
Time of achievement of upper value of the temperature range	70 min

SOME ASPECTS OF THE TECHNIQUE USED TO MEASURE TEMPERATURE BEHAVIOR OF THE WIDTHS AND SHIFTS OF A SPECTRAL LINE

Measurements were performed at the room temperature. The test cell was filled with pure water vapor at low pressure ($P_{H_2O} \leq 5$ Torr). The second cell was filled with a mixture of H_2O vapor of the same quantity with a buffer gas at the buffer gas pressure of 760 Torr. The gas mixture under study was prepared in a glass bulb of a vacuum station. The gas pressure inside the bulb was monitored with mercury and oil gauges. The bulb volume was connected to the thermal PA cell volume by a small glass tube. Since the gauges used to measure partial and total gas pressure in a mixing bulb were outside the PA cell and at the room temperature, we had to conduct preliminary test measurements of H_2O line broadening and shift caused by the gas pressure variation in the thermal cell.

Such measurements for 694.38-nm H_2O vapor absorption line were conducted in air at 373 K using two ways of filling the thermal PA cell with the gas medium under study. In the first way the PA cell was pumped out to the pressure less than 10^{-3} Torr and heated to 373 K prior to filling. Then it was filled with the prepared mixture of H_2O vapor and air. After that the measurements of the line width (γ) and shift (δ) started. In the second way of PA cell filling the cell was first filled and then heated to 373 K prior to measurements of γ and δ .

The results of test measurement presented in Table I show that the spread of measured values observed at different ways of the cell filling are within the limits of the experimental error.

TABLE I.

Way of filling the cell	Measured values at 373 K	
	$\gamma, \text{cm}^{-1} \cdot \text{atm}^{-1}$	$\delta, \text{cm}^{-1} \cdot \text{atm}^{-1}$
I	0.154 ± 0.005	0.013 ± 0.003
II	0.157 ± 0.005	0.013 ± 0.003

Errors in the gas temperature and pressure measurements inside the reference and measurement cells were shown (see, for example, Ref. 8) to be insignificant compared to those caused by the laser radiation nonmonochromaticity and error in its wavelength measurements.

MEASUREMENTS OF TEMPERATURE DEPENDENCE OF γ AND δ OF H_2O ABSORPTION LINES BROADENED BY AIR

A modified dual-channel PA spectrometer with the thermal cell was used to measure the temperature dependence of the width and shift of 694.38-nm H_2O vapor absorption line in air. Within the temperature range from 299 to 373 K, series of γ and δ measurements have been carried out at the following temperatures, fixed with the accuracy of ± 0.4 K: 303, 323, 352, 353, and 373 K. Results of these measurements are presented in Figs. 2 and 3. The fitting of the experimental results to the Voigt contour⁹ was used as the data processing procedure. As a result, the values of broadening and shift coefficients were obtained for every temperature mentioned above.

The function $\gamma(T)$ for the temperature range under study was described by a power law, proposed by W.S. Benedict and L.D. Kaplan¹⁰

$$\gamma(T) = \gamma(T_0) (T_0/T)^n, \tag{1}$$

where $T_0 = 293$ K. Similarly we have for shift

$$\delta(T) = \delta(T_0) (T_0/T)^{n'}, \tag{2}$$

where $\gamma(T_0)$ and $\delta(T_0)$ are the values of the broadening and shift coefficients at $T_0 = 293$ K.

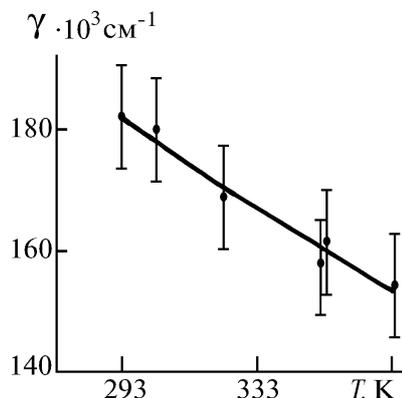


FIG. 2. Temperature dependence of the H_2O absorption line half-width (694.38 nm) in air. $P_{H_2O} = 5$ Torr and $P_{air} = 760$ Torr.

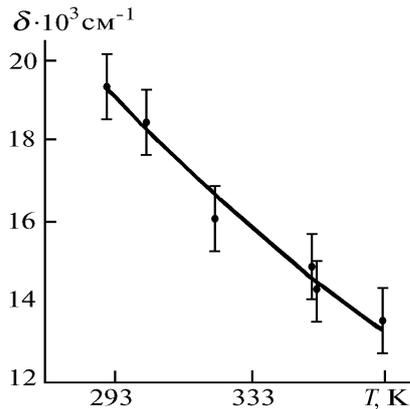


FIG. 3. Temperature dependence of the line center shift of the same line broadened by air. $P_{\text{H}_2\text{O}} = 5$ Torr and $P_{\text{air}} = 760$ Torr.

Thus, the determined average value of the exponent in Eq. (1), for 694.38-nm spectral line under study ($4_{14}-5_{15}$ transition of the 103 band) was 0.65 ± 0.15 , what well agrees with the corresponding value of $n = 0.6$ for analogous $4_{14}-5_{15}$ transition of the 301 band measured in Ref. 11. Average value of $n' = 1.53 \pm 0.15$ [in Eq. (2)] also agrees with the data from Ref. 11. Thus, the modified PA spectrometer allowed us to obtain reliable quantitative information about behaviors of width and shift at the temperature varying in the range from 290 to 400 K, what provides a solution to the inverse problems of remote sensing of the atmospheric water vapor.

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