

Influence of the instrumental function of an photoacoustic spectrometer on the accuracy of determining the H₂O continuum absorption coefficient at 14400 cm⁻¹

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It is shown that the excess absorption of radiation by water vapor recorded in the transmission microwindow near 14400 cm⁻¹ over its selective component is not connected with the spectrometer instrumental function.

In our previous paper¹ we have reported on the measurements of continuum absorption by water vapor in the visible spectral region by the photoacoustic (PA) laser spectroscopy method. The coefficient of continuum absorption by water vapor in the region near 14400 cm⁻¹ was determined as the difference between the absorption coefficient measured in the transmission window ($\nu = 14398.9$ cm⁻¹) and the coefficient of selective absorption calculated using line-by-line method.² The PA spectrometer was calibrated to the peak absorption by water vapor at the line centered at $\nu_0 = 14400.329$ cm⁻¹. The value of the continuum absorption coefficient k_{cont} at the total pressure of the water vapor and nitrogen mixture of $P_{\text{total}} = 1$ bar, partial water vapor pressure $P_{\text{H}_2\text{O}} = 1$ mbar and a temperature of $T = 295$ K was $k_{\text{cont}} = (0.53 \pm 0.18) \cdot 10^{-9}$ cm⁻¹, or 12 percent of the H₂O absorption measured in the transmission window and only 0.32 percent of the absorption at the line peak centered at $\nu_0 = 14400.329$ cm⁻¹.

Radiation non-monochromaticity (the instrumental function of the spectrometer) appears in an apparent broadening of the recorded absorption lines and a decrease of the recorded absorption at line centers.³ In this connection, the neglect of the PA spectrometer instrumental function in measurements of the continuum absorption coefficient by the method described in Ref. 1 would cause the excess of the absorption measured in the transmission microwindow over the calculated selective absorption. Moreover, this excess can erroneously be assigned to the continuum absorption.

In this paper, we demonstrate that the excess of the absorption recorded experimentally¹ in the transmission microwindow at 14400 cm⁻¹ over its selective component is not connected with the instrumental function of the PA spectrometer.

Assume, that in the considered spectral region $k_{\text{cont}} = 0$. In this case, while recording the absorption spectra with a pulsed PA spectrometer that enables us to record absorption by a gas against zero level of

the background,¹ we measure the spectral distribution of the parameter k_{eff} connected with the amplitude of the PA signal $U(\nu_1)$, with the laser pulse energy E , and the spectral distribution of the selective absorption coefficient for the i th line $k_i(\nu)$, by the following relation:

$$k_{\text{eff}}(\nu_1) = U(\nu_1) / (\alpha E) = \sum_i \int_{\Delta\nu_i} k_i(\nu) f(\nu_1 - \nu) d\nu \quad (1)$$

where, like in Ref. 1, summation is performed over the absorption lines that fall within the spectral interval of $\nu_1 \pm 25$ cm⁻¹. In Eq. (1), ν_1 is the wave number for the maximum of the pulsed laser radiation spectrum; α stands for the PA spectrometer sensitivity determined in calibration; the function f characterizes the laser radiation spectrum. According to the right-hand part of Eq. (1), $k_{\text{eff}}(\nu_1)$ is the absorption coefficient of the radiation that has the wave number ν_1 distorted by the spectrometer instrumental function f .

In our paper cited as Ref. 1, the radiation spectrum of a pulsed ruby laser recorded with a Fabry–Perot interferometer with the resolution not less than 0.003 cm⁻¹ consists of a single component and is described by the Gaussian function. The full width of the spectrum at half maximum ($2\gamma_1$) for some laser pulses varies from 0.035 to 0.045 cm⁻¹. Water vapor absorption lines are specified¹ by the Voigt contour⁴:

$$k_i(\nu) = \frac{k_i^{\text{max}} Y}{\pi} \int \frac{e^{-t^2}}{Y^2 + (X - t)^2} dt, \quad (2)$$

where for each i th line

$$k_i^{\text{max}} = \frac{S}{\gamma_D} \left(\frac{\ln 2}{2} \right)^{1/2}; \quad Y = \frac{\gamma_L}{\gamma_D} (\ln 2)^{1/2}$$

$$X = \frac{\nu - \nu_0}{\gamma_D} (\ln 2)^{1/2}; \quad \gamma_D = \frac{\nu_0}{c} \sqrt{\frac{2RT \ln 2}{N_A m}},$$

$$\gamma_L = \Gamma_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + \Gamma_{\text{N}_2} P_{\text{N}_2}.$$

In Eq. (2), k^{\max} is the absorption coefficient at line maximum; γ_D and γ_L are the Doppler and collisional line half-widths, respectively; R is the universal gas constant; N_A is the Avogadro constant; m is the mass of water molecule; T stands for the temperature; $P_{\text{H}_2\text{O}}$ and P_{N_2} are the experimental partial pressures of water vapor and nitrogen, respectively. In our calculations¹ we used the data on the intensities S and self-broadening coefficients $\Gamma_{\text{H}_2\text{O}}$ of water vapor absorption lines.⁵ The data on the coefficients of line broadening by nitrogen were taken from Ref. 6.

In the calculation of convolutions of spectral distributions of the absorption coefficients and the radiation spectrum by Eq. (1), the integration was performed within $\Delta\nu_1 = \pm 3\gamma_1$ about the maximum of the laser pulse radiation spectrum, where γ_1 is the radiation spectrum half-width at half maximum. Our additional calculations showed that for any of its wave numbers ν_1 , integration over any wider $\Delta\nu_1$ interval causes a change in the value of the integral in Eq. (1) not more than by 0.01 percent. The calculations by Eqs. (1) and (2) have been performed with the double accuracy, which reduces the error in the absorption coefficient calculated down to 0.04 percent.

An example of the measured spectral distribution $k_{\text{eff}}(\nu)$ (reported in Ref. 1) together with the calculated selective absorption spectrum for the H_2O –nitrogen mixture is shown in Fig. 1.

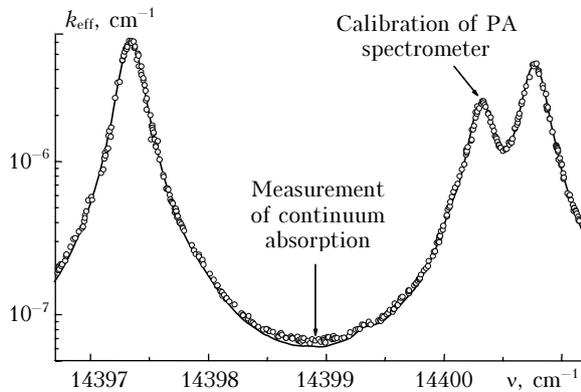


Fig. 1. Measured (circles) and calculated (solid line) water vapor absorption spectrum near the ruby laser generation line. Partial pressure of water vapor $P_{\text{H}_2\text{O}} = 15$ mbar, total pressure of the water vapor–nitrogen mixture $P_{\text{total}} = 1$ bar, $T = 295$ K. The width of the instrumental function of the PA spectrometer $2\gamma_1 = (0.035\text{--}0.045)$ cm^{-1} (experiment) and $2\gamma_1 = 0.040$ cm^{-1} (calculation).

The errors in measuring the absorption coefficients (including the error of absorption coefficients calculations, the PA spectrometer calibration error, the PA signal measurement error, the errors of laser pulse energy, and in the partial gas pressures in a cell) do not exceed the size of the symbols (circles) used in Fig. 1 to show the measurement results. In the calculations of the effective absorption coefficient in the region we took the average

value of the ruby laser radiation spectrum width, which was $2\gamma_1 = 0.04$ cm^{-1} . We have performed binding of the experimental and calculated data in the following way. The experimental data for the line with $\nu_0 = 14400.329$ cm^{-1} in the region of $(\nu_0 \pm \gamma_L)$ were approximated by the Voigt contour. Then, we found the scaling factor (the sensitivity α) superposing the maxima of the fitted and calculated contours.

In our experiment, we measured the relative shift of the ruby laser radiation wavelength accurate to 0.002 cm^{-1} , which, in superposing the maxima, automatically provided binding of the experimental and calculated spectra on the x axis. From Fig. 1 we can see that binding the experimental and calculated spectra at one point, at the maximum of the line with $\nu_0 = 14400.329$ cm^{-1} gives a good agreement between the experimental and calculated data in the central parts of the profiles of two other absorption lines of H_2O . In line wings, experimental data exceed the calculated results. For $\nu = 14398.90$ cm^{-1} , the excess is 12.9 percent.

Figure 2 illustrates the dependences of the calculated parameter k_{eff} on the laser radiation spectrum width for absorption at line maximum frequency $\nu_0 = 14400.329$ cm^{-1} and in the transmission microwindow near $\nu = 14398.9$ cm^{-1} .

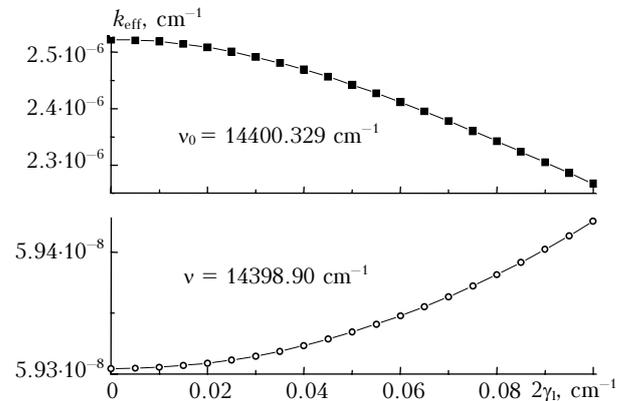


Fig. 2. Dependences of the calculated parameter k_{eff} at line maximum ($\nu_0 = 14400.329$ cm^{-1}) and in the transmission microwindow ($\nu = 14398.90$ cm^{-1}) on the laser radiation spectrum width. The calculation is performed for $P_{\text{H}_2\text{O}} = 15$ mbar, $P_{\text{total}} = 1$ bar, and $T = 295$ K.

Analysis of these dependences shows that at variations of the spectrometer instrumental function width ($2\gamma_1$) in the region of the experimental values, i.e., from 0.035 to 0.045 cm^{-1} , the error of k_{eff} calculations at line maximum varies from $+0.5$ to -0.5% . For $\nu = 14398.90$ cm^{-1} , the error in calculated k_{eff} in the considered region of $2\gamma_1$ values makes just ± 0.008 percent.

The effect of inaccurate setting of the spectrometer instrumental function width on the errors in determining the continuum absorption coefficient by the method described in Ref. 1 is

demonstrated in Fig. 3, where we show the dependence of the relative error in determining the parameter k_{cont} for $\nu = 14398.90 \text{ cm}^{-1}$ on the laser radiation spectrum width.

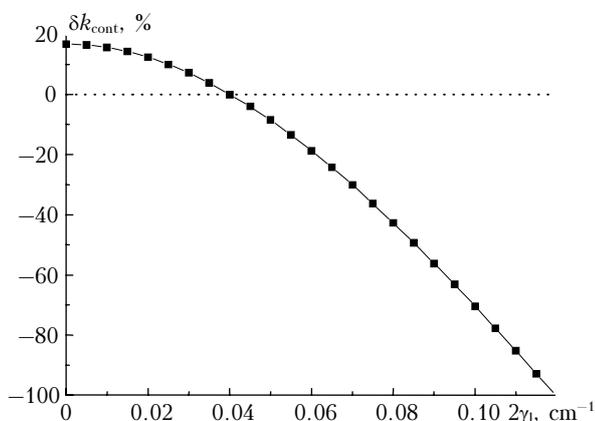


Fig. 3. Dependence of the relative error in determining the continuum absorption coefficient $\delta k_{\text{cont}} = 100 \cdot [k_{\text{cont}}(2\gamma_l) - k_{\text{cont}}(0.04)] / k_{\text{cont}}(0.04)$ near $\nu = 14400 \text{ cm}^{-1}$ on the laser radiation spectrum width.

From Fig. 3 we can see that for an average experimental value of $2\gamma_l = 0.04 \text{ cm}^{-1}$, the k_{cont} determination error due to the instrumental function equals zero. Having varied the instrumental function width $2\gamma_l$ from 0.035 to 0.045 cm^{-1} , we obtain the error in the k_{cont} determination changes from $+3.8$ to -4.0% . In the case of negative error values, the result for k_{cont} is underestimated, and vice versa, for the positive error the k_{cont} value is overestimated. Since in the limiting case, at $2\gamma_l = 0$ (the monochromatic radiation), the parameter k_{cont} reaches its maximum

increasing no more than by 17 percent, we may assert that the excess absorption of the ruby laser radiation by water vapor mixed with nitrogen over its selective component is not caused by the effect of the instrumental function of our PA spectrometer.

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References

1. A.B. Tikhomirov, I.V. Ptashnik, and B.A. Tikhomirov, *Opt. Spektrosk.* (2006) (to be published).
2. A.A. Mitsel, I.V. Ptashnik, K.M. Firsov, and B.A. Fomin, *Atmos. Oceanic Opt.* **8**, No. 10, 847–850 (1995).
3. A.N. Zaidel, G.V. Ostrovskaya, and Yu.I. Ostrovsky, *Techniques and Practices of Spectroscopy* (Nauka, Moscow, 1972), 376 pp.
4. V.E. Zuev, *Propagation of Visible and Infrared Radiation in the Atmosphere* (Halsted Press, New York, 1974).
5. L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian Jr., K. Chance, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, and G. Wagner, *J. Quant. Spectrosc. Radiat. Transfer* **96**, No. 2, 139–204 (2005).
6. P.-F. Coheur, S. Fally, M. Carleer, C. Clearbaux, R. Colin, A. Jenouvrier, M.-F. Merienne, C. Hermans, and A.C. Vandaele, *J. Quant. Spectrosc. Radiat. Transfer* **74**, No. 4, 493–501 (2002).