RECONSTRUCTION OF BROADENING AND SHIFT COEFFICIENTS FROM THE DATA ON THE DERIVATIVE OF AN ABSORPTION LINE SHAPE MEASURED WITH A DOUBLE FREQUENCY LASER

V.A. Kapitanov, M.Yu. Kataev, and O.Yu. Nikiforova

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

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In this paper we present some results of reconstructing the coefficients of absorption line broadening and shift by the air or acetone pressure for several rotational lines of 401 *and* 500 *vibrational bands of* H_2O *molecule from the measurements of photoacoustic signal derivative using a dual-channel PA spectrometer equipped with a dye laser.*

Dye laser and two photo-acoustic cells are the main components of the spectrometer (see Ref. 1). Double-frequency mode of the laser operation was used. This mode of operation of a spectrometer with linear dye laser offers some advantages.

First, the sensitivity threshold of the spectrometer in absorption coefficient measurements is increased by more than two times as compared to the single-frequency mode of operation owing to an increase of the laser output power.

Second, a double frequency dye laser is more simple in operation than a single-frequency one because narrowing of the output spectrum of such a laser is achieved by the use of two selective components such as a birefringent filter and a thin Fabry-Perot etalon with a relatively low reflectance from their surfaces whereas three selective components are used in the case of a single-frequency laser.

Third, spectrometers with a double-frequency and single-frequency linear dye laser exhibit almost the same spectral resolution in measurements of the position of an absorption line center and half-width of the line. Preliminary results on the half-width of absorption line and shift of its center from experimentally obtained spectra are presented in Refs. 2 and 3. In this paper, a treatment of the absorption lines investigated within 401 and 500 vibrational bands of H_2O molecule for visible spectrum (0.59 μm) is performed. Interest in this spectral range results from the following concepts. First, visible spectrum is poorly investigated in terms of spectroscopy. Second, data on absorption as well as on broadening and shift of spectral lines by pressure in this spectral range are used in lidar and passive atmospheric sounding.[4,5]

PA spectrometer records the spectrum in the following way. Tunable laser radiation passes through two PA cells filled with a gas (or a mixture of a gas under study with a buffer gas) to be investigated at different pressure. Then, PA signals from the cells are defined as the ratio of the electric signal from a microphone, which controls pressure changes in the cells, to laser energy. Those signals are functions of the convolution of the laser spectrum and an absorption line shape of the gas to be examined at a given pressure. Derivatives of the signals with respect to frequency are recorded since derivatives are more sensitive to changes in the line shape parameters than the signals themselves. Use of a double-frequency laser radiation to record absorption lines results in a complicated and peculiar waveform of a signal (see Fig. 1*c*) which enables one to more reliably detect weak lines. Besides, the difference of two laser mode frequencies being completely determined by the parameters of a laser cavity makes it possible to determine the scale of the frequency axis when processing the measurements.

Note that the ratio between the intensities of two laser lines can slightly vary from measurement to measurement. Therefore, the data presented in Fig. 1*a* should be considered only as a qualitative illustration of the laser spectrum observed. For this reason, characteristics of laser radiation are additional fitting parameters resulting in an increase of processing time and extra errors in the values of half-widths and shifts.

When processing the experimental results, an absorption line was assumed to be described by the Voigt profile $V = V(\nu)$. Taking into account two laser lines with the frequency difference $\Delta\nu$ and the ratio of their intensities C (see Fig. 1*a*), PA signal in each cell can be written as[6]: $U = A(V(\nu) + C\,V(\nu + \Delta\nu))$. (Here the constant A describes the efficiency of conversion of energy absorbed by a gas into electric signal from a microphone.) Since in the measurements presented derivative of PA signal was recorded instead of the signal itself, the latter can be simulated by the following expressions:

$$F_1(\nu) = A_1 \left(\frac{\partial V(\nu - \nu_0(P_1), \gamma(P_1))}{\partial \nu} + \right.$$
$$\left. + C \frac{\partial V(\nu - \nu_0(P_1) - \Delta\nu, \gamma(P_1))}{\partial \nu} \right);$$

$$F_2(\nu) = A_2 \left(\frac{\partial V(\nu - \nu_0(P_2), \gamma(P_2))}{\partial \nu} + \right.$$
$$\left. + C \frac{\partial V(\nu - \nu_0(P_2) - \Delta\nu, \gamma(P_2))}{\partial \nu} \right), \qquad (1)$$

where A_1 and A_2 are the coefficients of conversion in the first and second channels of the spectrometer, respectively; ν_0 is the frequency corresponding to the center of an absorption line; $\gamma_1 = \gamma(P_1)$, $\gamma_2 = \gamma(P_2)$ are Lorenz half-widths of the lines in the first and the second PA cells, respectively (Doppler half-width γ_D is suggested to be equal to 0.022 cm^{-1} in the vicinity of 0.59 μm). The difference in the frequency of the absorption line centers obtained in different channels of the spectrometer determines the shift by pressure: $\Gamma = \nu_0(P_1) - \nu_0(P_2)$.

Some methods of reconstructing the absorption line parameters from measurements are available. These methods are based on the assumption that the signal can be described by the following equation:

$$y(\nu) = \int\limits_{-\infty}^{\infty} A(\nu - \nu')\ V(\nu')\ d\nu' + \xi(\nu), \qquad (2)$$

where $A(\nu - \nu')$ is the instrumental function, $V(\nu')$ is the true spectral shape of the absorption line, $\xi(\nu)$ is the measurement noise.

A great number of approaches to solution of the equation (2) is known (see, for example, Refs. 7–12). In many methods, when estimating parameters of $F(\nu)$ model function, the rms deviation of the experimental data y from $F(\nu) = f(\nu, p)$ function is taken to be a measure of accuracy of the fitting parameters,

$$L(p) = \sum_{i=1}^{N} (y(x_i) - f(x_i, p))^2. \qquad (3)$$

Here $p = \{p_1,..., p_m\}$, m is the number of parameters.

Other measures, such as weighted average, over measurements, absolute value and so on, can be used as well. Then, the criterion for making decisions on the searching for such values of the parameters p when the measure used satisfies some condition is chosen. For instance, in the case of the measure (3), parameters p are selected so that $L(p)$ is reduced to a minimum. That is precisely the approach which is used in a widely employed least squares method (LSM). But it does not always happen that measure (3) results in a precise estimation of the parameters p of the model function. Nevertheless, it is possible to obtain optimal estimations using LSM with a “good” initial approximation. That is why this method is widely used in practice.

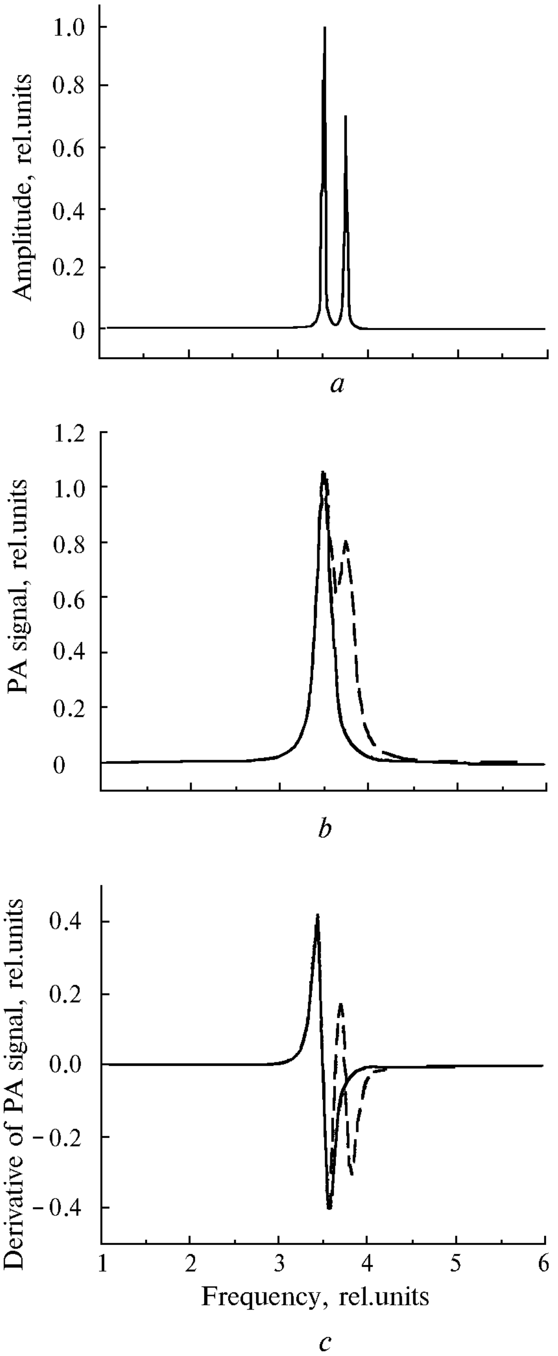


FIG. 1. Influence of a double-frequency mode of measurements (a) on PA signal in the case of Doppler shape (b) and its derivative (c). Solid and dashed lines correspond to single- and double-frequency modes of measurements, respectively.

We have considered different methods and their modifications$^{7-13}$ for determining such parameters of spectral line shape as half-width and shift. Unfortunately, experimental error prevents application of the most “fast” gradient methods since the instrumental noise, nonlinearity of model function and a large number of fitting parameters (5–8) reduce the efficiency of these methods.

Classical methods such as the least squares method and modified method of direct search (MMDS) were chosen to process the experimental data obtained. These methods were used due to their reasonable stability to experimental errors and acceptable rate of convergence. When fitting according to LSM, the function to be minimized has the following form:

$$\sum_{i=1}^{N} [(y_1(x_i) - F_1(x_i, p_1))^2 + $$
$$+ (y_2(x_i) - F_2(x_i, p_2))^2] \to \min . \tag{4}$$

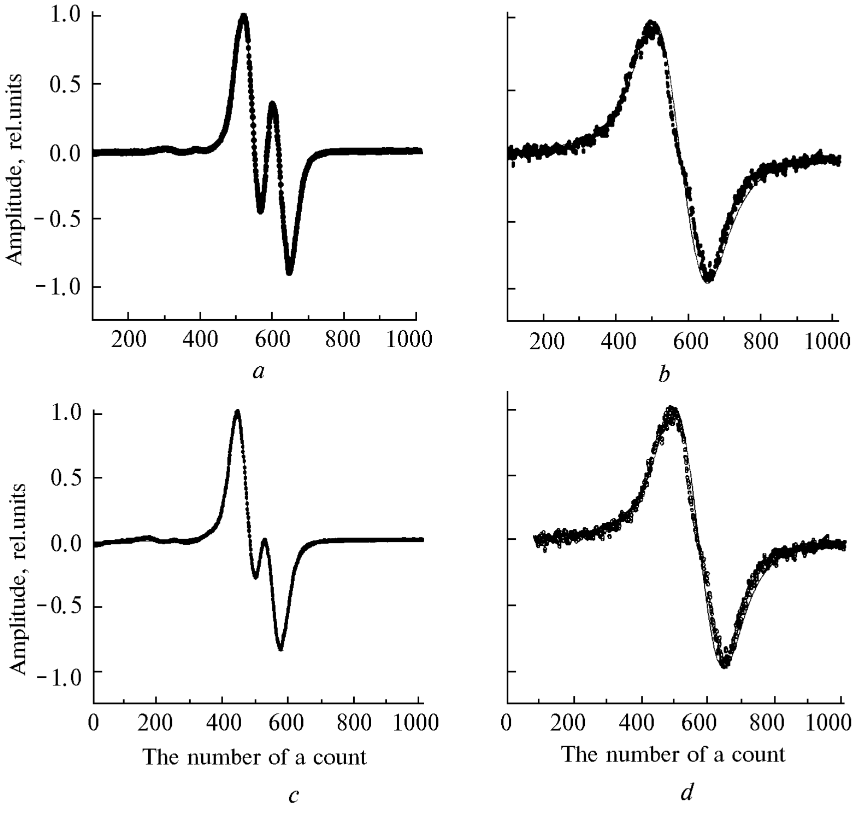
Here N is the sample size (a number of points on a line shape recorded); y_1, y_2 are signals measured in the first and second cells, respectively; F_1, F_2 are the values of model function (1) which correspond to the chosen values of parameters p_1 and p_2. Coefficient of conversion in the first channel A_1, parameters of laser radiation C and $\Delta\nu$, parameters of the line to be investigated ν_0 and γ_1 are used as a set of fitting parameters p_1. A set of parameters p_2 (A_2, C, $\Delta\nu$, ν_0, γ_2, Γ) differs from p_1 by the values of the coefficient of conversion in the cannel (A_2) and Lorentz half-width of the line (γ_2) since a gas or gas mixture pressure in the PA cell of the second channel is different. Besides, the set includes shift of the line center, Γ. Attention should be drawn to the fact that the use of $\Delta\nu$ as a fitting parameter enable its value to be expressed in relative frequency units, whereas a known absolute value of that parameter provides a possibility of converting experimentally obtained γ_1, γ_2, and Γ values into absolute frequency units (cm^{-1} or MHz).

Application of LSM makes us to pay proper attention to the choice of the initial approximation since model functions F_1 and F_2 are highly nonlinear and their expansion into a series over their arguments with an accuracy to linear terms can be obtained only in a small vicinity of the solution.

The second method, namely, MMDS depends only slightly on the choice of the initial approximation. This method is based on minimizing, independently for each channel, the following function:

$$\sqrt{\sum_{i=1}^{N} (F_j(x_i, p_j) - y_j(x_i))^2} \to \min; \quad j = 1, 2 . \tag{5}$$

Parameters C, ν_0 and $\Delta\nu$ for the second channel are considered to be already determined. The minimizing (5) is performed in two steps. The first one involves the search for a descent trajectory and the second one consists in the search for a solution in the direction selected.



a *b*

c *d*

FIG. 2. Results of experimental data fitting by model functions (1) at low (a, b) and high (c, d) gas pressure. Points correspond to a measured derivative of the PA signal, solid line corresponds to a model derivative with the parameters reconstructed.

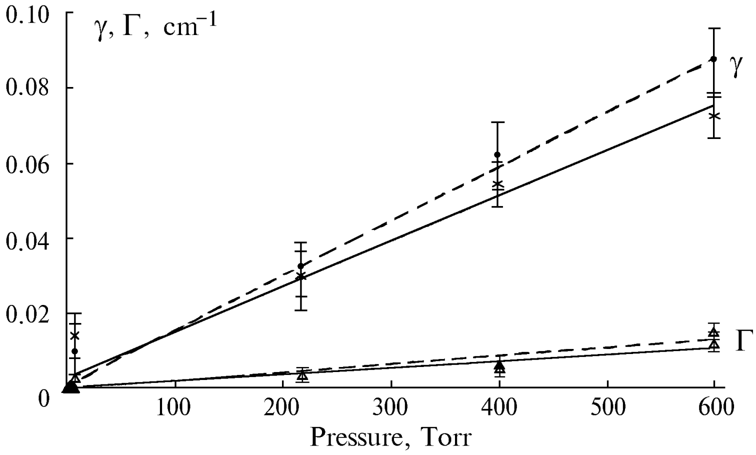


FIG. 3. Lorenzian half-width (γ) and shift of absorption line center (Γ) against pressure. Solid and dashed lines are calculated using LSM and MMDS, respectively.

TABLE I.

Wavelength, nm	Vibrational band	$(J'\,K_a'\,K_c')$ – $(J\,K_a\,K_c)$	Coefficients, MHz·Torr			
			c_b	c_s	c_b	c_s
			Air		Acetone	
588.3914	401	616–717	3.3 ± 0.7	– 1.5 ± 0.1	–	–
588.5977	401	505–606	2.9 ± 0.5	– 1.0 ± 0.1	–	–
588.9637	401	414–515	1.8 ± 0.6	– 1.0 ± 0.2	(7.5 ± 2.0)*	0.5 ± 0.3
589.1660	500	303–414	1.8 ± 0.6	– 0.42 ± 0.1	5.2 ± 0.5	3.8 ± 0.4
589.8166	401	212–313	2.9 ± 0.2	– 0.54 ± 0.2	–	–
589.9919	500	212–303	3.7 ± 0.6	– 0.58 ± 0.2	–	–
590.1468	401	101–202	–	–	10.2 ± 0.5	3.0 ± 2.0
591.9644	401	322–321	–	–	6.9 ± 0.5	3.8 ± 0.5
593.2092	401	212–111	3.4 ± 0.4	– 0.7 ± 0.2	–	–

Starred data require improvement of the model (1).

In Ref. 2 we have proposed a combination of the methods discussed above. MMDS is used to find initial approximation and LSM is used to improve the solution obtained. But in the present paper this combined method is not used since it takes a long time to process a large set of experimental data and, thus, LSM and MMDS were used in parallel. Figure 2 depicts examples of the signals measured and corresponding model functions. Quality of fitting by the functions F_1 and F_2 for two measurements is demonstrated in Figs. 2*a* and *b* and Figs. 2*c* and *d*. Curves presented in Figs. 2*a* and *c*, and Figs. 2*b* and *d* correspond to low and high pressure, respectively. As Fig. 2 shows, the presence of two lines in the output laser spectrum is hardly noticeable at a sufficiently high pressure. Comparison between the results obtained with these methods is presented in Fig. 3, where dependences of half-width of 212–111 line of 401 band of H_2O molecule and shift of the line center by air pressure are shown. Although the results obtained with the methods are close within experimental error, as is shown in Fig. 3, the broadening and shift coefficients (the angle of inclination of the corresponding straight lines) slightly differ. Since physical reasons for this difference are not clear, two methods were used in parallel to process the set of experimental data and the results obtained were averaged. Coefficients of broadening (Γ_b) and shift (Γ_s) by pressure of air and acetone for several rotational lines from 401 and 500 vibrational bands of H_2O molecule are listed in Table I. The data in the fifth column of Table I improve the results reported in Ref. 3. Note that these methods of data processing allow one to calculate not only shift coefficients available previously, but broadening coefficients as well.

Based on the investigations performed, we have come to the following conclusions:

1. LSM and MMDS can serve as independent means for estimating shift and broadening coefficients

of the absorption lines to be investigated. However, in our opinion, if additional processing time is available, these methods should be used in parallel and the parameters reconstructed should be averaged to improve their reliability.

2. Since the errors in the frequency scale estimation make a contribution to the error in the reconstructed values of the half-width and shift, it is desirable to control independently the laser parameters C and $\Delta\nu$.

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