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CHARACTER OF THE CHANGE IN THE VOIGT CONTOUR OF A WEAK ABSORPTION LINE IN A LASER SPECTROMETER WITH AN ANALYTICAL CAVITY

O. M. Vokhnik* and P. V. Korolenko UDC 543.422

The variation in the shape of the Voigt convolution profile in a spectrometer for measuring weak absorption consisting of a frequency tunable laser and an external analytic resonator is studied. It is found how the characteristics of the convolution and the parameters of the resonator affect the reproduction of the shape and width of the absorption line. The effect of absorption saturation on the accuracy of measuring the weak absorption coefficient is discussed.

Keywords: *Voigt contour, optical resonator, spectrometer, frequency-tunable laser, absorption saturation, quality of spectral measurements.*

High-quality absorption spectroscopy, which makes it possible to record the presence in different media of substances in low concentrations, is required in many areas of modern life: medicine, ecology, safety systems and in scientific applications [1–3]. One of the realizations for schemes for a laser spectrometer for measuring weak absorption combines the action of a tunable diode or quantum-cascade laser and an external analytic resonator in which the test medium is placed. Detection of a temporal signal after passing of the resonator makes it possible to record an absorption spectrum without a traditional spectral instrument. This scheme (known as ICOS, integrated cavity output spectroscopy) and its modifications have been studied in many papers (e.g., [4–7]); nevertheless a number of features of the recording of optical spectra require refinement. In particular, during recording of a spectrum, under the influence of various physical factors the shape of a recorded absorbed line may vary. The change includes broadening of the line, as well as distortion of the contour of a spectral line. It has been shown previously [8] that for a Gaussian form factor of a line both factors show up, while a Lorentzian line retains its shape. Here its spread is larger than that of a Gaussian line for other equal conditions. For the case when the form factor of an absorption line is the Voigt convolution of Gaussian and Lorentzian contours the change in the line shape as the radiation passes through an analytic resonator was not examined, although a similar shape is typical for many media.

The purpose of this paper is to clarify with numerical modeling the features of changes in Voigt profiles after passage of the probe radiation through an analytic resonator with an absorbing medium placed inside it. Primary attention is devoted to the case when the width of the surrounding Gaussian profile is comparable to the width of the Lorentzian profiles included in the convolution. These kinds of contours are seldom seen in the literature, although a similar form of spectral line is characteristic of media that are often used in practice.

A scheme for calculating the characteristics of radiation passing through an analytic resonator based on combining its output amplitude of partial beams repeatedly reflected from mirrors [9] was used. The analysis was done in the most general form — in the approximation of plane waves using dimensionless quantities, which makes it possible to identify the most general factors determining the results of the measurements. Adding the amplitudes of the partial waves in accordance with the geometrical progression formula gives an amplitude S at the output of the resonator of

$$S(k) = \frac{AT_1T_2e^{i\left[\delta(k)d+\Phi\right]}p(k)}{1 - R_1R_2e^{2i\left[\delta(k)d+\Phi\right]}p(k)^2}, \quad (1)$$

*To whom correspondence should be addressed.

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where k is the discrete time with a sampling interval d; A is the amplitude of the input wave; Φ is its phase; T_1 and T_2 are the amplitude transmission coefficients of the resonator; R_1 and R_2 are their amplitude reflection coefficients (we neglect the losses at the mirrors; $T_{1,2} = \sqrt{1 - R_{1,2}^2}$; $\delta = 2\pi l v$ is the rate of change of the phase in a single passage of a resonator of length l; $v = df/dk$ is the rate of retuning of the frequency f of the laser. The rate of increment in the phase is assumed proportional to time (as a rule, the frequency varies with a linear dependence), which makes it possible to write $\delta = xk$, where x is rate of change of the frequency. The absorption of the medium is specified in Eq. (1) by the transmission coefficient $p(k) = \exp[-p'(k)\alpha - i\varphi_n(k)]$, which depends on the form factor $p'(k)$ of the absorption line, the absorption coefficient α at the line center, and additionally, on the phase advance $\varphi_n(k)$. The phase advance $\varphi_n(k)$ arises from the change in the refractive index n in the region of the absorption line; for small absorption coefficients, it is negligibly small and we neglect it in the following. Four different form-factors $p'(k)$ are used in the calculations. They are Voigt contours with different ratios between the width ΔG of the envelope of the Gaussian profile $p'_G(k) = \exp\left(\dfrac{(k-k_0)^2}{\Delta^2}\right)$ and the width ΔL of the Lorentz components in the convolution $p'_\mathrm{L}(k) = \dfrac{\Delta\sqrt{\ln 2}}{(k-k_0)^2 + (\Delta\sqrt{\ln 2})^2}$. Here k_0 is the time the frequency of the laser passes through the line center and Δ characterizes the width.

The form-factors $p'_\mathrm{V}(k)$ of the Voigt profiles are calculated using the expression [10]

$$p'_\mathrm{V}(k) = \int_{\xi_1}^{\xi_2} p'_\mathrm{L}(\xi, k)\, p'_\mathrm{G}(\xi, k_0)\, d\xi \,. \tag{2}$$

The width ΔG of the Gaussian envelope was assumed to be fixed, and the ratio of the width ΔL of the Lorentzian contours took values of $\Delta L/\Delta G = 2.0$ (a Lorentz profile 2 times wider than the Gaussian envelope), 1.0 (the Lorentzian and Gaussian widths equal, and 0.5 and 0.2 (the Lorentz width 2 and 5 times smaller than the Gaussian width).

Figure 1 shows the form-factors $p'_\mathrm{V}(k)$ of the Voigt profiles. The width ΔV and shape of the Voigt convolutions depend substantially on the ratio $\Delta L/\Delta G$. When the Lorentz contour width of the Lorentz profile in the convolution is substantially smaller than the width of the Gaussian envelope (curve 4), the shape of the convolution and its width are very close to the Gaussian envelope. As the ratio $\Delta L/\Delta G$ increases the width ΔV of the convolution and its profile differs substantially from the Gaussian (curves 2 and 3), and for $\Delta L/\Delta G = 2.0$ the shape of the convolution is practically Lorentzian and its width ΔV is a factor of ~2.5 greater than the width of the Gaussian envelope. The expression in [11] approximately describes the ratio between the widths of the Voigt ΔV, Gaussian ΔG, and Lorentzian ΔL profiles:

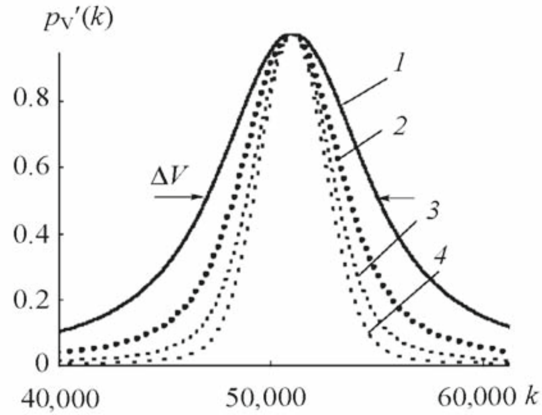
$$\Delta V \approx 0.5346\Delta L + \sqrt{(\Delta G)^2 + 0.2166(\Delta L)^2} \tag{3}$$

for the calculated profiles with an accuracy of 0.1%.

In the calculations of the amplitude, width, and shape of the emission line passing through an analytic resonator were determined as functions of the absorption coefficient α, which varied from 0.0005 to 0.02. The reflection coefficients of the resonator mirrors, R_1 and R_2, which determine the cavity Q, were assumed to be the same, i.e., $R_1 = R_2 = R$, and equal to 0.98, 0.99, 0.995, and 0.999, with $T_1 = T_2 = \sqrt{1 - R^2}$. The input amplitude A of the probe beam was set at unity.

When scanning the frequency of the driver laser at the resonator output a sequence of resonance peaks is formed corresponding to its longitudinal modes. Near the center of the absorption line the amplitudes of the resonance peaks $|S(k)|$ decrease, and tracing their maxima yields a curve which can be used to judge the shape of the line and the absorption coefficient. The difference Y between the values of $|S(k)|$ far from the absorption line and in the center of the line is essentially the amplitude of the measured signal and characterizes the sensitivity of the spectrometer. The width Δ' of the line was determined at the half-height of the curve obtained by tracking the maxima of the resonance peaks. The line broadening u was estimated as the ratio of Δ' to the width ΔV of the initial form-factor $p'_\mathrm{V}(k) : u = \Delta'/\Delta V$.

As the calculations show, the amplitude profile of the absorption line determined at the outlet of the resonator varies: its width increases, while the shape changes from the initial shape. It has been found that the broadening of the line is determined by such factors as the cavity Q, the absorption coefficient α, and the shape of the profile of the convolution $p'_\mathrm{V}(k)$ and it is greater when α is greater and the cavity Q is greater. The effect of the shape of the convolution on the broadening of the line is represented by the dependences $u(\alpha)$ for a maximum cavity Q ($R = 0.999$) (Fig. 2). It can be seen



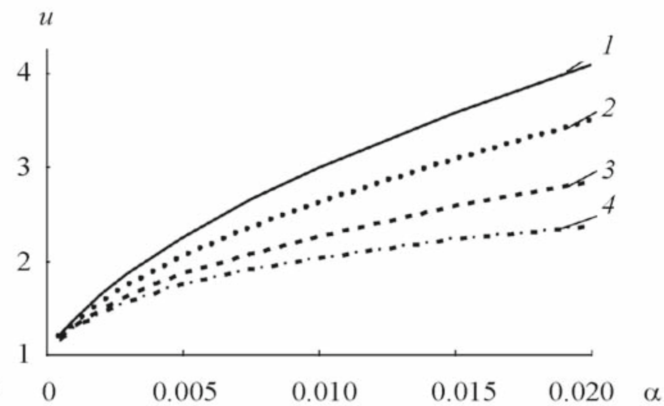


Fig. 1. Voigt profiles used in the calculation: $\Delta L/\Delta G$ = 2.0, 1.0, 0.5, and 0.2; the amplitudes of the profiles are assumed equal to unity

Fig. 2. The increase in the width of a line after passage through an analytic resonator: 1) practically Lorentzian shape of the Voigt profile ($\Delta L/\Delta G$ = 2.0); 2, 3) shapes intermediate between Lorentzian and Gaussian profiles ($\Delta L/\Delta G$ = 1.0, $\Delta L/\Delta G$ = 0.5); 4) almost Gaussian shape of the Voigt profile ($\Delta L/\Delta G$ = 0.2).

that the greatest broadening is for an absorption spectrum for which the form-factor of the line essentially coincides with Lorentzian (curve 1) and the least, is for one with a Gaussian profile (curve 4). In the intermediate cases (curves 2 and 3) the broadening is greater when the line shape is closer to Lorentzian. Similar $u(\alpha)$ dependences occur after passage of resonators with a lower Q, but the values of $u(\alpha)$ in this case are noticeably lower. For example, when R = 0.999 the maximum calculated line width is greater than than the width of the initially specified line by a factor of 4.1 (curve 1), while when R = 0.955 the same convolution yields a two-fold magnification, and for R = 0.98 the width increases by a factor of 1.3.

After passing through an analytic cavity the line profile not only increases but also is distorted: the shape of the calculated contour differs noticeably from the $p'_V(k)$ dependence. The distortion of the shape, like the broadening of the line, shows up more strongly when the cavity Q and the absorption coefficient α are higher.

The form-factor $p'_V(k)$ also influences the degree of distortion; the distortion is greater when the form-factor $p'_V(k)$ is closer to Gaussian. Figure 3a shows the difference between the calculated profile of the convolution after passage through an analytic cavity (curve 2) on the form-factor of this line at the input into the cavity (curve 1). The calculation was done for a Voigt convolution with a ratio of $\Delta L/\Delta G = 2.0$, a reflection coefficient $R = 0.999$, and an absorption coefficient α = 0.02. For convenience of comparison of the line profiles the initial form-factor is given for the same width as the transmitted profile. It is clear that after passage of the resonator the wings of the profiles differ, while the central part of the passing profile becomes wider than the original. For the form-factors of convolutions close to Lorentzian ($\Delta L/\Delta G \geq 2$) the distortion in the line shape is absent, regardless of the Q-factor of the cavity and the absorption coefficient.

The forms of the convolutions following passage of analytic resonators for which the ratio $\Delta L/\Delta G$ is very small (≤0.05) and the form-factor $p'_V(k)$ is essentially Gaussian have an interesting feature after passage of an analytic resonator. When they are compared compared with the result of the passage of an ordinary Gaussian profile through the same kind of resonator (Fig. 3b) is is clear that the Voigt convolutions have a small, but well resolved broadening in the wings. It can be explained by the fact that in the wings of the original Voigt convolution Lorentzian profiles are always present and it is their strong broadening after passage of the cavity that changes the shape compared to Gaussian.

Thus, it follows from the calculations that the profiles $p'_V(k)$ of the Voigt convolutions, which are close to Lorentzian do not change shape after passing a cavity, but substantially increase in width. As the form-factor $p'_V(k)$ changes and it approaches Gaussian, for which substantially less broadening and noticeable distortion [8] are seen, the shape of the convolution line has less broadening and is more distorted.

In measurements with an external cavity it should be noted that a large increase in the intracavity power compared to the initial level requires a certain correspondence between the cavity Q and the measured absorption coefficient α.

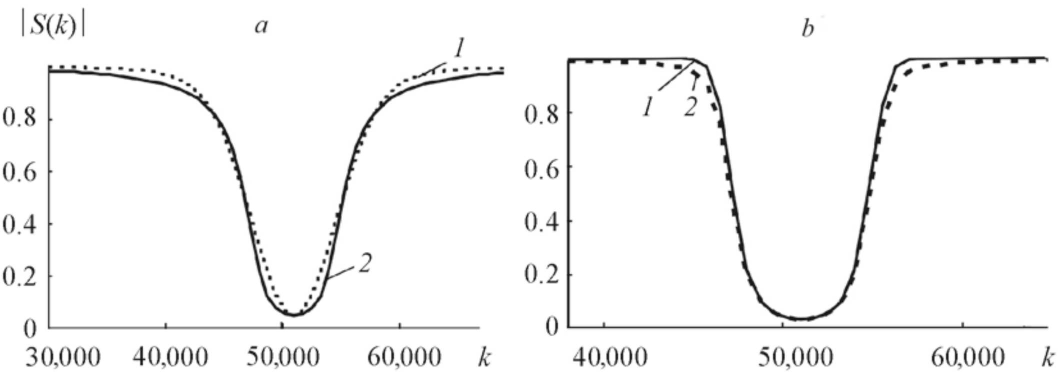


Fig. 3. Form-factors of an absorption line to (1) and after passage of an analytic cavity (2) (a) as well as comparison of a Gaussian profile (1) and a Voigt convolution for $\Delta L/\Delta G = 2.0$ (2) after passage of a cavity (b).

On one hand, a correct measurement of small α requires that the signal amplitude be sufficient for its reliable measurement (this requires an increase in the cavity Q) and on the other, the increase in the Q must be accompanied by conservation of the linear range of the measurement of the signal amplitude, which distorts the measurement results [8].

The above described features of the change in the shape of the recorded spectrum line were established in the approximation of a weak signal without accounting for the effects of saturation absorption. However, in a number of cases for high intensity of the input signal and an intracavity field these effects may affect the spectral characteristics. Let us make a qualitative estimate of this influence for a Lorentzian line. It is known that upon saturation the profile of a homogeneously broadened line that remains Lorentzian increases in width by a factor of $\sqrt{1 + (I/I_S)}$, where I is the radiant intensity and I_S is the saturation parameter, which depends on the characteristics of the material being studied [10]. Here the actual absorption coefficient of the medium in the cavity is $\alpha_L = \alpha(1 + I/I_S)$.

A high level of radiative intensity inside the cavity is observed when the cavity Q is high. Thus, for $R = 0.999$ the power of the radiation in the cavity taking into account the presence of the two opposed waves is higher by three orders than the output power. Assuming that for this power $I/I_S = 1$, it can be established that for these α the corrections owing to accounting for saturation of absorption are negligible ($\leq 10\%$). This is explained by the oppositely directed effect of the factors associated with the reduction in the absorption coefficient and the broadening of the line.

The features of the change in the characteristics of radiation after it passes through the analytic cavity of a spectrometer for measuring weak radiation have been studied. The form-factor of the absorption line is presented in the form of a Voigt convolution of Gaussian and Lorentzian lines of comparable width. It was found that after passage of a cavity the width of the detected line increases and its form changes relative to the initial shape more strongly when the cavity Q and absorption coefficient of the test medium are higher. It has been shown that the shape of a Voigt convolution influences the character of the change: the closer its profile is to Lorentzian, the greater its broadening and the less the distortion of the shape. If the shape of the convolution is close to a Gaussian envelope, then the broadening is reduced while the distortion is enhanced. It was found that after a specified Voigt convolution profile essentially coinciding with Gaussian is recorded, it has differences from Gaussian owing to substantial broadening of external Lorentzian components entering the convolution.

REFERENCES

1. E. V. Stepanov, *Diode Laser Spectroscopy and the Analysis of Molecule-Biomarkers* [in Russian], Fizmatlit, Moscow (2009).
2. V. N. Ochkin, *Physics Uspekhi*, **65** (10), 1071–1103 (2022).
3. T. Zhang, G. Zhang, X. Liu, G. Gao, and T. Cai, *J. Appl. Spectrosc.*, **87**, No. 4, 674–679 (2020).
4. D. S. Baer, J. B. Paul, M. Gupta, and A. O'Keefe, *Appl. Phys. B*, **75**, 261–265 (2002).
5. A. O'Keefe, J. J. Scherer, and J. B. Paul, *Chem. Phys. Lett.*, **307**, 343–349 (1999).
6. P. V. Korolenko, V. V. Lagunov, I. V. Nikolaev, V. N. Ochkin, S. N. Tshai, and A. N. Yatskevich, *Sov. J. Quantum Electron.*, **46**, No. 3, 255–258, (2016).

7. V. V. Lagunov, I. V. Nikolaev, and V. N. Ochkin, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, **246**, Article ID 119060 (2021).
8. O. M. Vokhnik, P. V. Korolenko, and R. T. Kubanov, *J. Appl. Spectrosc.*, **89**, No. 1, 114–117 (2022).
9. M. Born and E. Wolf, *Principles of Optics*, Cambridge University Press, 7th edn. (1999).
10. R. H. Pantell and H. E. Puthoff, *Fundamentals of Quantum Electronics*, John Wiley, New York, London, Sydney, Toronto (1969).
11. J. J. Olivero, and R. L. Longbothum, *J. Quant. Spectrosc. Rad. Transf.*, **17**, No. 2, 233–236 (1977).