



International Journal of Emerging Technologies in Computational and Applied Sciences (IJETCAS)

www.iasir.net

Evaluation of the Uncertainty in Spectral Peak Location Case Study: Symmetrical Lines

J. Dubrovkin

Computer Department, Western Galilee College
2421 Acre, Israel

Abstract: The dependences of the relative peak shifts of Gaussian and Lorentzian symmetrical doublets on the peak separation were evaluated theoretically. It has been shown that these dependences are well described by the eighth-order polynomial over the inverse of the line separation. The shifts for asymmetrical Gaussian, Lorentzian, and Voigt doublets were calculated numerically. The qualitative patterns were obtained and some abnormal phenomena were revealed.

Keywords: spectroscopy; peak identification; peak location uncertainty; peak profiles.

I. Introduction

Peak location of spectral lines and bands is one of the most important quantitative parameters, widely employed in theoretical and applied spectroscopy [1]. For example, classical identification of unknown elements and chemical compounds is usually performed by comparing the experimentally measured peak positions with those found in the standard library. The shifts of the peak positions are indicative of intra- and intermolecular interactions and changes of the external parameters (e.g., temperature). In this connection, the evaluation of the peak location uncertainty is of exceptional importance. However, one should regard the existence of two types of errors that arise in solving this problem. One type of errors is connected with the computational procedure [2] and instrumental factors [3], while the errors of the other type are due to overlapping of the component spectra, which may cause apparent shifts [4]. Errors of the first type can be easily eliminated by simple mathematical treatment [2, 3] and careful recalibration of the spectrometer. In contrast to this, the resolution of overlapping bands is a complicated task [5]. Therefore, from the practical point of view, it seems reasonable, first of all, to evaluate the upper limits of the apparent shifts and decide whether sophisticated computer methods should be further used in this particular case.

The impact of spectral overlapping on the peak positions is usually evaluated qualitatively. The peak positions of resolved maxima are often assumed to be accurate values. Quantitative evaluation of the apparent shifts of peak positions in Gaussian and Lorentzian doublets, as well as in their ideal derivatives and in those obtained numerically, was performed only for a few particular cases by means of computer modeling [6, 7]. In these works, the dependence of the shift on the parameters of the overlapping lines was not established.

The goal of this work was evaluating the peak position uncertainty caused by overlapping lines. Gaussian, Lorentzian, and Voigt profiles were studied. In what follows, for the sake of simplicity, term "line" is used for short of phrase "line and band".

The standard algebraic notations are used throughout the article. All calculations were performed and the plots were built using the MATLAB program.

II. Theory

A. Models

Consider a doublet which maxima are located at the points $-x_0$ and x_0 , respectively:

$$D(x) = F(x + x_0) + RF((x - x_0)/r), \quad (1)$$

where $F(x)$ is the doublet line; $x = \beta i/w$; β is the parameter of the line shape; $i = -m, -m + 1, \dots, 0, \dots, m - 1, m$; w is the full line width at half-maximum; $x_0 = \beta\delta/2$; $\delta = \Delta/w$ is the relative separation of the doublet components; $\Delta = 2i_0$ is the absolute separation; i_0 is the position of the line maximum; R and r are the relative intensity and the relative width of the second doublet line, respectively.

The following line shape functions were studied in this work:

a. Gaussian function [1]:

$$F_G(x) = \exp(-x^2), \quad (2)$$

where $\beta_G = 2\sqrt{\ln 2}$.

b. Lorentzian function [1]:

$$F_L(x) = 1/(1 + x^2), \quad (3)$$

where $\beta_L = 2$;

c. Voigt function [1]:

$$F_V(x) = \int_{-\infty}^{\infty} F_G(x't_G)F_L((x - x')t_L)dx', \quad (4)$$

where $t_G = w/w_G$ and $t_L = w/w_L$; w_G, w_L are the full widths of Gaussian and Lorentzian lines, respectively. The width of the Voigt profile [8] is

$$w_V \approx 0.5346w_L + \sqrt{0.2166w_L^2 + w_G^2}. \quad (5)$$

B. Relative shift

The relative shift of the line position is usually measured with respect to the line width. However, the widths of overlapping lines can be evaluated very approximately [6, 9]. Therefore, in this work, we chose to calculate the shifts with respect to the separation of the doublet components, which can be readily measured visually. In this case, the relative shift of the resolved doublet peak for the i -component has the form:

$$\xi_i = (x_{mi} - (-1)^i x_0) / 2x_0, \quad (6)$$

where $i = 1, 2$; x_{mi} is the point at which the derivative of Eq. 1 is zero:

$$D^{(1)}(x_{mi}) = 0 \quad (7)$$

In the neighborhood of x_m , $D^{(1)}(x)$ is positive on the left, while on the right of x_m it is negative.

Unfortunately, the analytical solution of Eq. 7 exists only in the particular cases of symmetrical Gaussian and Lorentzian doublets ($R = r = 1$) (see Appendix B):

$$\xi_G \approx -1.2039A^4 + 2.0285A^3 - 1.7449A^2 + 0.6336A - 0.0801, \quad (8)$$

$$\xi_L \approx -0.1391A^4 + 0.3359A^3 - 0.4152A^2 - 0.0685A - 0.0088, \quad (9)$$

where $A = 1/2x_0^2$, the values of A ranging from 0.89 to 0.32 and from 1.39 to 0.22 for Eqs. 8 and 9, respectively.

In all other cases, Eq. 7 can be solved only numerically, but, as we have found, the $\xi(x_0)$ dependences obtained analytically and numerically are very close.

Since, for a symmetrical doublet, $D^{(1)}(0) = 0$, the merged doublet lines display the same absolute shift x_0 at the resolution limit and below the limit. The value of the relative shift, $|\xi| = 0.5$, does not depend on the separation of the doublet components. For separations larger than the resolution limit, the maxima of the first and the second lines are located at $x_{m1} < 0$ and $x_{m2} > 0$, respectively. At the resolution limit of an asymmetrical doublet, $D^{(1)}(x_{rl}) = 0$, where x_{rl} is located near the zero point. Below the resolution limit, the merged doublet lines appear as a single line with a shoulder (Fig. 1). If the maximum of the first line is resolved, then $x_{m1} < x_{rl}$ and, consequently, the second line manifests itself as the right shoulder of the doublet (Fig. 1a). If the maximum of the second line is resolved, then $x_{m2} > x_{rl}$ and the left shoulder relates to the first line (Fig. 1b). In both cases, the maximum of the resolved line is shifted. It has been found (Appendix 3) that for $R = r$ the absolute relative shift

$$|\xi| = 0.5|1 - (r - 1)/(r + 1)| \quad (10)$$

does not depend on the separation of the doublet peaks.

III. Results of Computer Modelling and Discussion

A. Equal-width lines ($r = 1$)

It can be seen from Eqs. 8 and 9 that near the resolution limit of symmetrical doublets ($R = 1$), the relative shift is inversely proportional to a very high power of the separation of the doublet components (Fig.2).

1. On the strength of symmetry, the line shift dependences on the line separation (Fig.2) are related as:

$$\xi_1^{(r=1)}(R, \delta) = -\xi_2^{(r=1)}(1/R, \delta) \quad (11)$$

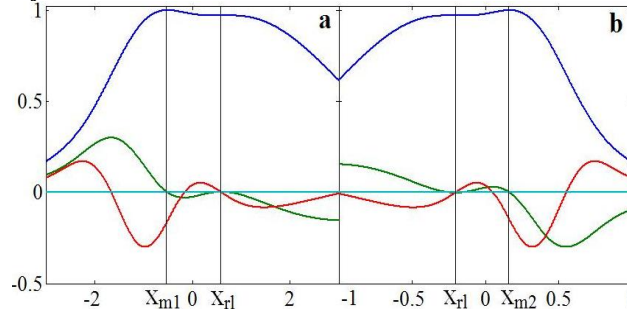
2. Although the more intensive second line (larger R values) causes larger shifts of the first line, its own shifts decrease. Thus, if $R_1 > R_2$ (Fig.2),

$$|\xi_1^{(r=1)}(R_1, \delta)| > |\xi_1^{(r=1)}(R_2, \delta)| \quad (12)$$

$$|\xi_2^{(r=1)}(R_1, \delta)| < |\xi_2^{(r=1)}(R_2, \delta)| \quad (13)$$

3. Slowly decaying interfering wings of the Lorentzian lines result in larger shifts than the corresponding quickly decaying Gaussian wings (Fig. 3):

Figure 1 Asymmetrical Gauss doublet and its derivatives near resolution limit.



Doublet (blue), the 1st (green), and the 2nd (red) derivatives. (a) $R=3, r=1/3, \delta=1.2$. (b) $R=1/3, r=3, \delta=0.4$.

$$|\xi_{1L}^{(r=1)}(R, \delta)| > |\xi_{1G}^{(r=1)}(R, \delta)|, R \gtrsim 1, \delta \gtrsim 1.2 \quad (14)$$

$$|\xi_{2L}^{(r=1)}(R, \delta)| > |\xi_{2G}^{(r=1)}(R, \delta)|, R \gtrsim 2.8 \quad (15)$$

Owing to symmetry,

$$|\xi_{1L}^{(r=1)}(R, \delta)| > |\xi_{1G}^{(r=1)}(R, \delta)|, R \lesssim 1/2.8 \quad (16)$$

$$|\xi_{2L}^{(r=1)}(R, \delta)| > |\xi_{2G}^{(r=1)}(R, \delta)|, R \lesssim 1, \delta \gtrsim 1.2 \quad (17)$$

The effect described by Eqs. 16 and 17 is significantly enhanced by increasing the intensity of the interfering line.

4. In the cases of both equal-width and non-equal-width doublet lines, the plot of the $\xi(R, \delta)$ dependences for the Voigt profile lies between the corresponding plots for Gaussian and Lorentzian doublets (Fig.4).

5. The shifts of doublet peaks near the resolution limit are presented in the Table. The obtained results show that the relative shift may be as large as more than 30% of the peak separation.

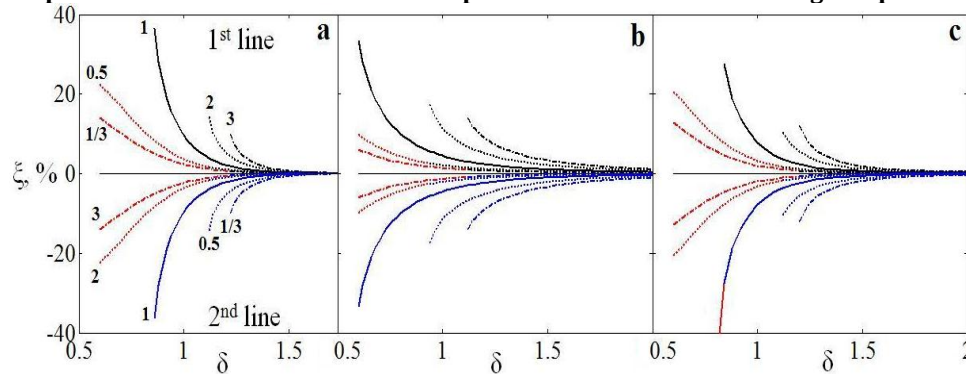
B. Non equal-width lines ($r \neq 1$)

1. If $r > 1$, then the second line, which is more intensive and wider (larger R value), causes larger shifts of the first line; however, its own shifts decrease (Fig. 5). This effect is significantly enhanced with the second line broadening. If $r < 1$, then the first line, which is more intensive and wider (smaller R value), causes larger shifts of the second line; however, its own shifts decrease. This effect is significantly enhanced the first line widening. The abnormal behaviour of the $\xi(\delta)$ plots (horizontal regions) is explained by Fig. 6. The plots in this figure show the positions of the zero points of the doublet first derivatives (Appendix 3, Eq. A21), which correspond to the first line maxima ($x_{m1} = \delta/4$), δ increasing from the resolution limit ($\delta = 1.2$) to the point of the $\xi_1(\delta)$ dependence discontinuity ($\delta = 1.6$) (Fig. 5, $r = 3$, a). In this case, $\xi_1(\delta) = 25\%$. The discussed anomaly disappears for $\delta > 1.6$.

2. For a given separation, the broader second line causes larger relative shifts of both lines. Such effect is most pronounced near the resolution limit of the Lorentzian doublets than of the Gaussian doublets (Table). The more intensive second line increases the first line shift; however, its own shifts decrease (Figs. 7, 8).

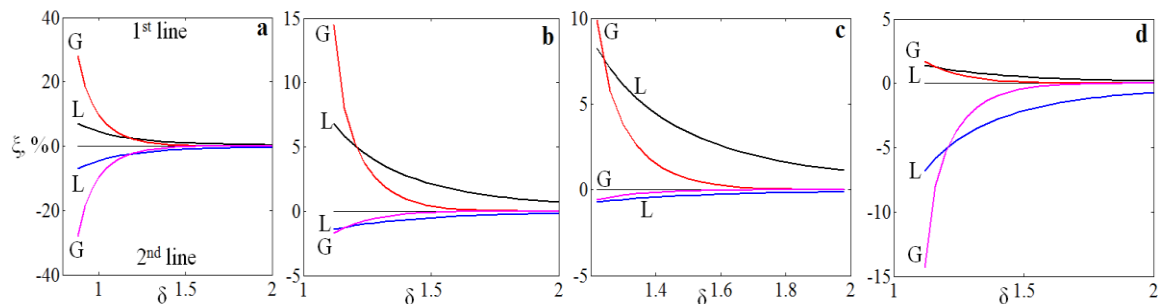
3. In certain particular cases, increasing the separation of the doublet lines does not lead to the gradual increase of the resolution (Fig. 9). In the open separation interval ($0.2 < \delta < 0.4$), only the right peak can be observed, while in the closed interval [$0.4 \leq \delta \leq 0.48$], two peaks are resolved. However, for $0.48 < \delta < 0.60$, only the left peak can be found because the value of the first derivative at the peak location is slightly different from zero. At the endpoints, both the first and the second derivatives are equal to zero (Figs. 9c, e). This abnormal behaviour may greatly complicate peak identification, particularly, in the presence of noise.

Figure 2 Dependences of relative shifts on line separation for doublets consisting of equal-width lines.



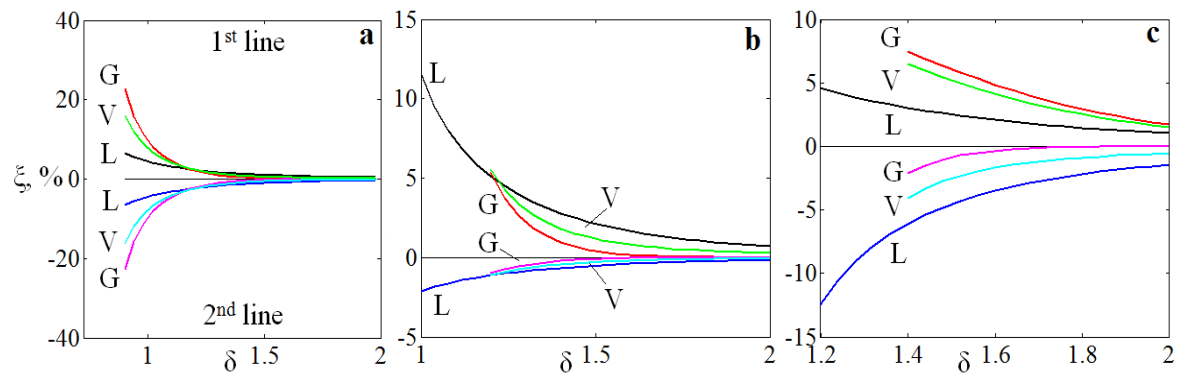
(a) Gaussian, (b) Lorentzian, and (c) Voigt lines; $w_L/w_G = 0.3$. The red curves lie below the resolution limit. The values of R are indicated next to the curves.

Figure 3 Comparison of the relative shift dependences on the line separation for doublets consisting of equal-width lines.



Gaussian (G) and Lorentzian (L) lines. $R = 1(a), 2(b), 3(c), 0.5(d)$.

Figure 4 Comparison of the relative shift dependences on the line separation for doublets consisting of Gaussian, Lorentzian, and Voigt lines.



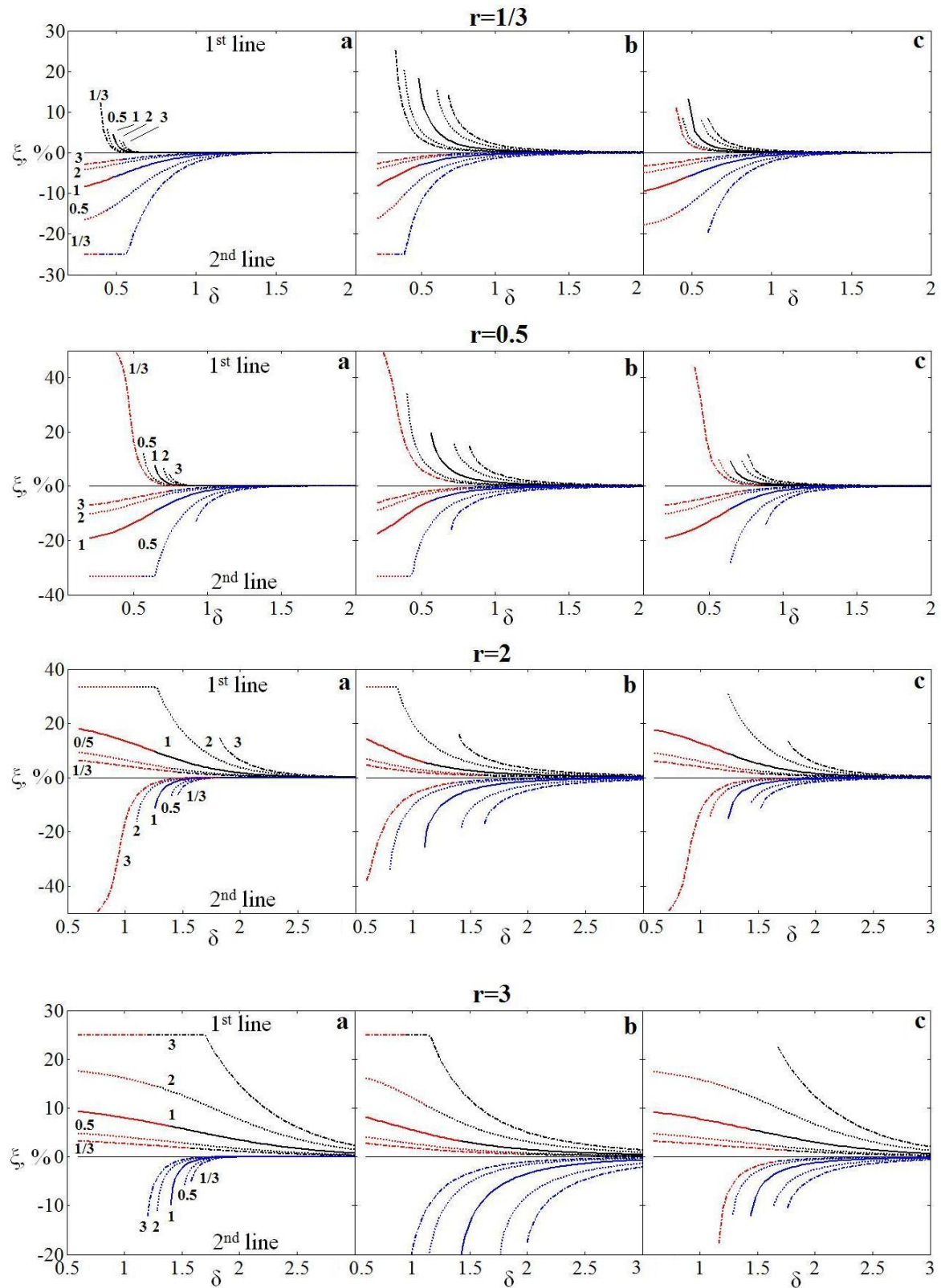
Gaussian (G), Lorentzian (L), and Voigt (V) lines; $w_L/w_G = 0.3$. (a) $R = 1$, $r = 1$; (b) $R = 2$, $r = 1$; (c) $R = 1$, $r = 2$.

Table 1: The shifts of the doublet peaks near the resolution limit.

R	1			0.5			1/3			2			3		
r	δ	$\xi_1, \%$	$-\xi_2, \%$	δ	$\xi_1, \%$	$-\xi_2, \%$	δ	$\xi_1, \%$	$-\xi_2, \%$	δ	$\xi_1, \%$	$-\xi_2, \%$	δ	$\xi_1, \%$	$-\xi_2, \%$
1	0.86	36.5	36.5	1.12	1.7	14.3	1.22	0.56	9.8	1.12	14.3	1.7	1.22	9.8	0.56
	0.60	33.5	33.5	0.94	2.6	17.4	1.12	0.94	14.1	0.94	17.4	2.6	1.12	14.1	0.94
	0.84	27.5	27.5	1.12	1.7	10.4	1.20	0.72	12.1	1.12	10.4	1.7	1.20	12.1	0.72
0.5	0.64	7.8	9.3	0.56	12.2	33.3	0.92	0.01	12.8	0.70	6.5	3.4	0.74	4.5	1.9
	0.56	19.7	5.4	0.40	34.2	33.3	0.70	1.8	15.9	0.72	15.6	1.4	0.82	14.7	0.62
	0.64	9.4	8.3	0.54	14.4	28.2	0.88	0.33	14.1	0.72	9.4	2.8	0.76	11.7	1.5
1/3	0.48	4.6	6.1	0.44	5.9	14.1	0.40	12.2	25.0	0.52	3.1	2.7	0.54	2.7	1.7
	0.48	18.3	3.1	0.38	20.3	10.4	0.32	25.2	25.0	0.60	15.5	0.95	0.68	14.2	0.46
	0.48	13.2	5.8	0.44	8.5	14.0	0.40	11.1	19.6	0.56	8.0	2.2	0.60	8.5	1.3
2	1.26	9.6	11.2	1.40	3.4	6.5	1.46	2.0	6.3	1.10	33.3	16.4	1.82	14.6	0.01
	1.10	5.6	25.9	1.42	1.4	18.2	1.62	0.64	17.1	0.80	33.3	34.2	1.40	15.9	1.8
	1.24	8.9	15.2	1.44	2.8	9.1	1.52	1.5	11.3	1.08	33.6	14.1	1.76	13.6	0.33
3	1.40	6.3	9.9	1.52	2.8	5.7	1.58	1.7	4.9	1.28	14.4	11.1	1.20	25.0	12.2
	1.42	3.2	21.5	1.76	1.0	20.8	2.00	0.48	17.6	1.12	10.6	23.9	0.94	25.0	30.9
	1.44	5.7	12.0	1.64	2.3	10.0	1.76	1.3	10.3	1.28	13.9	11.8	1.06	25.1	17.7

For each value of r , the calculated parameters for Gaussian, Lorentzian, and Voigt doublets are shown in the 1st, 2nd, and 3rd rows, respectively. Small errors are highlighted in bold.

Figure 5 Comparison of the relative shift dependences on the line separation for doublets consisting of non-equal-width lines.



Gaussian (a), Lorentzian (b), and Voigt (c) lines ($w_L/w_G = 0.3$). Red curves lie below the resolution limit. The values of R are indicated next to the curves.

Figure 6 Asymmetrical Gaussian doublets and its derivatives at and above the resolution limit.

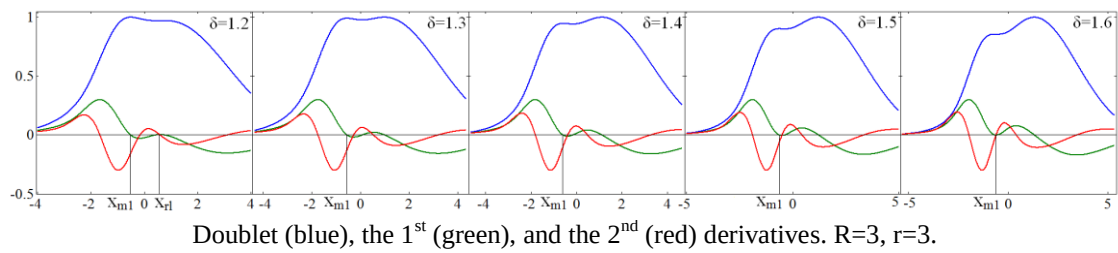


Figure 7 Comparison of the relative shift dependences on the line separation for doublets consisting of the non-equal-width lines.

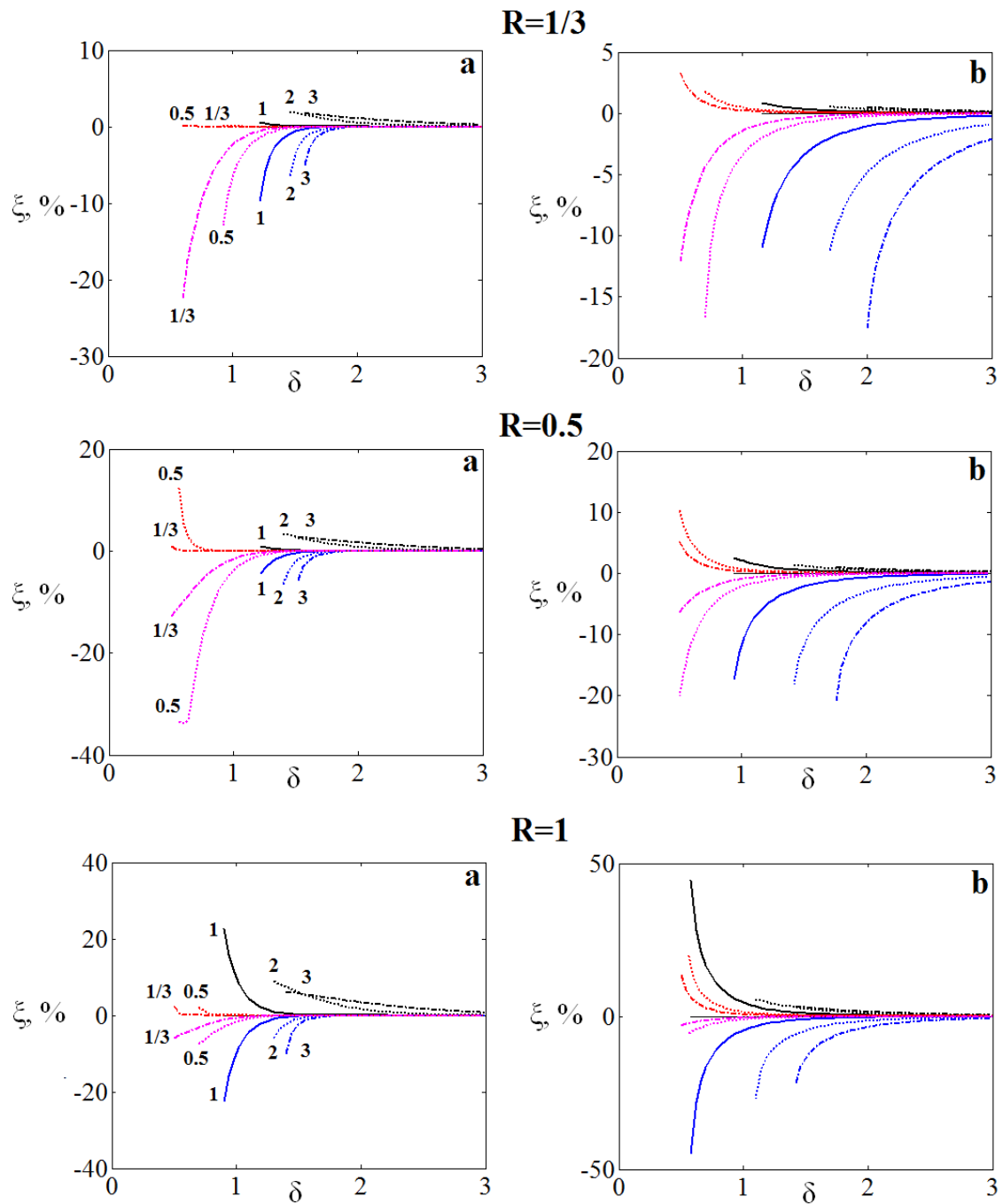
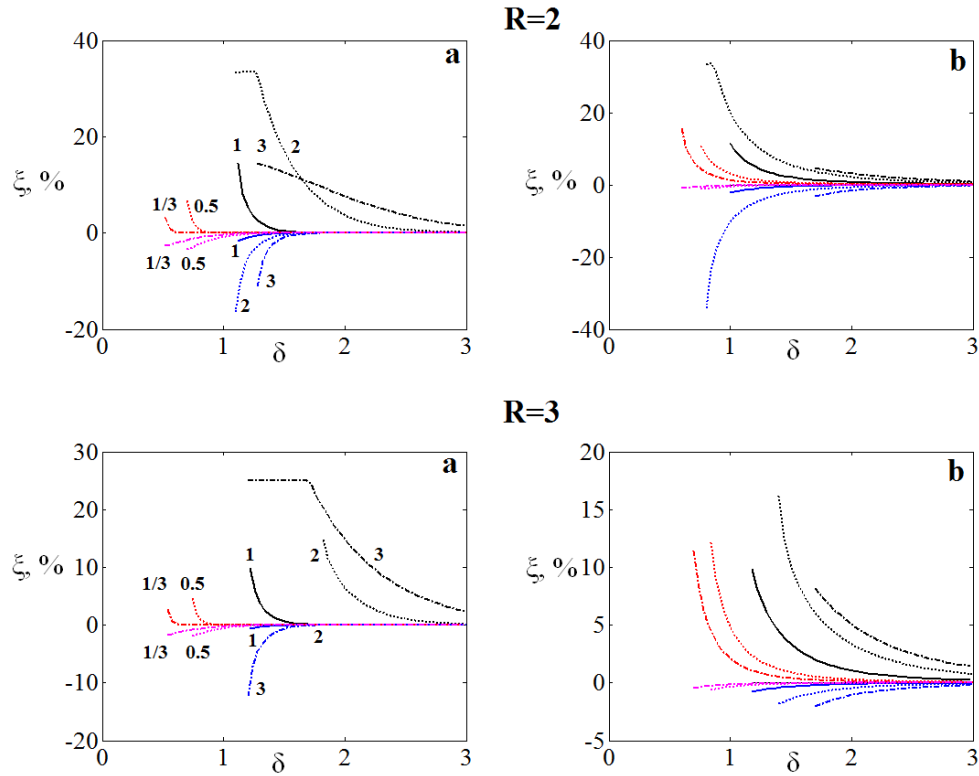
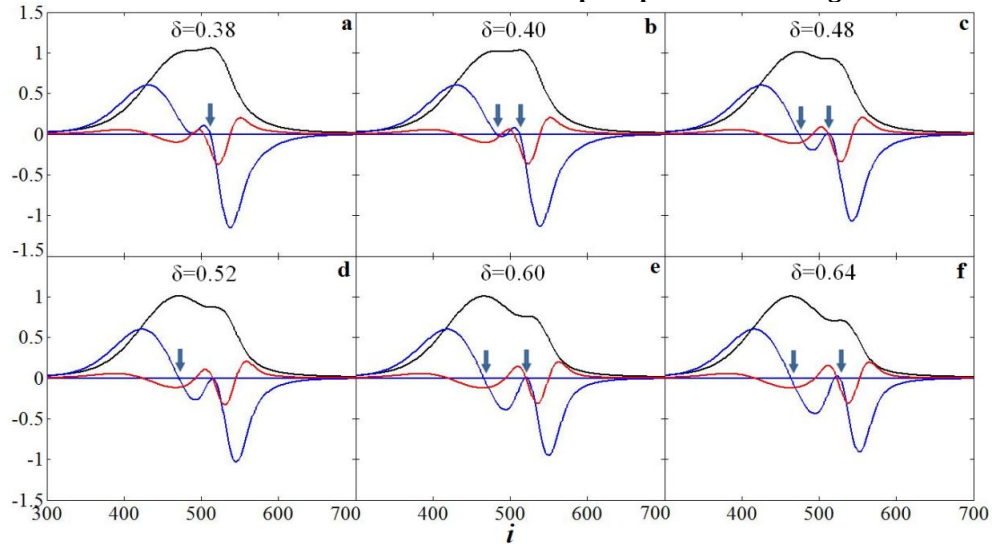


Figure 8 Comparison of the relative shift dependences on the line separation for doublets consisting of the non-equal-width lines.



Gaussian (a) and Lorentzian (b) lines. The values of r are indicated next to the curves.

Figure 9 Anomalous effects of the identification of the peak positions for Voigt doublets.



Doublet (black), the 1st (blue), and the 2nd (red) derivatives. $R = 1/3$, $r = 1/3$.

Appendix

1. Calculation of the peak shifts a symmetrical Gaussian doublet

For a symmetrical Gaussian doublet ($R = r = 1$), Eq. 7 has the following form after eliminating the common factor:

$$(x + x_0) \exp(-(x + x_0)^2) + (x - x_0) \exp(-(x - x_0)^2) = 0 \quad (A1)$$

Since $\exp(-x^2) \neq 0$ and $\exp(-x_0^2) \neq 0$, it follows from Eq. A1 that

$$\frac{y}{A} = \frac{\exp(y) - \exp(-y)}{\exp(y) + \exp(-y)}, \quad (A2)$$

where $y = 2xx_0$, $A = 1/2x_0^2$.

The trivial solution of Eq. A2, $y = 0$, is the central point of the doublet. The other roots of transcendental Eq. A2 can be found using a most precise approximation of the exponents based on continued fractions [10]:

$$\exp(y) = 1 + \frac{y}{-\frac{y}{2} + T}, \quad (A3)$$

where $T = (1 + k_1y^2)/(1 + k_2y^2)$, $k_1 = 0.0999743507186$, $k_2 = 0.0166411490538$. By substituting Eq. A3 into Eq. A2, the following cubic equation over $z=y^2$ is obtained:

$$2AT^2 - 2T + Az/2 = 0 \quad (A4)$$

Since the direct solution of Eq. A4 is very complicated, we used quadratic approximations in the range of the variable, $x_0 = 2\sqrt{\ln 2}$ ($0.45 \div 0.75$), being of practical relevance:

$$T = q_1 z^2 + q_2 z + q_3, \quad T^2 = q_4 z^2 + q_5 z + q_5, \quad (A5)$$

where $q_1 = T''/2 = k_2(k_2 - k_1)$, $q_2 = T' \approx k_1 - k_2$, $q_3 = T(0) = 1$, $q_4 \approx 1.75q_1^2 + 3q_1q_2 + 2q_1q_3 + q_2^2$, $q_5 \approx 2q_2q_3$, $q_6 = 1$.

Coefficients q_4 and q_5 were calculated by reducing the polynomial T^2 degree using the telescopic shift of the Lanczos power series expansion [11].

Thus we arrive at the final equation:

$$az^2 + bz + c = 0, \quad (A6)$$

where $a = q_1 + Aq_4$, $b = (0.5 + q_5)A + q_2$, and $c = q_3 + Aq_6$.

The positive solution of Eq. A6 is

$$z_m = \frac{-b + \sqrt{Q_1 A^2 + Q_2 A + Q_3}}{2a}, \quad (A7)$$

where $b = 0.8451A - 0.1650$, $a = 0.002257 + 0.004580A$, $Q_1 = 0.6778$, $Q_2 = -0.2602$, and $Q_3 = 0.04529$.

The relative shift (Eq. 6) now has the form:

$$\xi = \frac{1}{2}(A\sqrt{z_m} - 1) \quad (A8)$$

A simplified form of Eq. A8 was obtained using polynomial approximation (the MATLAB function *polyfit*):

$$\xi = -1.2039A^4 + 2.0285A^3 - 1.7449A^2 + 0.6336A - 0.0801, \quad (A9)$$

where $A = 0.89 \div 0.32$.

2. Calculation of the peak shifts for a symmetrical Lorentzian doublet

After eliminating the common factor, Eq. 7 for a symmetrical Lorentzian doublet ($R = r = 1$) has the form:

$$\frac{(x+x_0)}{(1+4(x+x_0)^2)^2} + \frac{(x-x_0)}{(1+4(x-x_0)^2)^2} = 0 \quad (A10)$$

The trivial solution of Eq. A10, $x = 0$, is the central point of the doublet. The other roots of Eq. A10 can be found from the equality

$$x^4 + Bx^2 + C = 0, \quad (A11)$$

where $B = (1 + 4x_0^2)/2$ and $C = (1 - 8x_0^2 - 48x_0^4)/16$.

The positive solution of Eq. A11 is

$$x = 2x_0\sqrt{2Z - Z^2}, \quad (A12)$$

where $Z = \sqrt{1 + A/2}$ and $A = 1/2x_0^2$.

The relative shift (Eq. 6) is

$$\xi = \frac{1}{2}(\sqrt{2Z - Z^2} - 1) \quad (A13)$$

A simplified form of Eq. A13 was obtained using polynomial approximation (the MATLAB function *polyfit*):

$$\xi_L = -0.1391A^4 + 0.3359A^3 - 0.4152A^2 - 0.0685A - 0.0088, \quad (A14)$$

where $A = 1.39 \div 0.22$.

3 Calculation of the zero point of the first derivative of an asymmetrical doublet in certain particular cases

In the cases of asymmetrical Gaussian and Lorentzian doublets, Eqs. A1 and A10 have the forms:

$$(x + x_0) \exp(-(x + x_0)^2) + (R/r^2)(x - x_0) \exp(-(x - x_0)^2/r^2) = 0 \quad (A15)$$

$$\frac{(x+x_0)}{(1+4(x+x_0)^2)^2} + \frac{(R/r^2)(x-x_0)}{(1+4(x-x_0)^2/r^2)^2} = 0, \quad (A16)$$

respectively.

The above two equations have trivial solutions if two conditions are fulfilled:

$$x + x_0 = -(R/r^2)(x - x_0) \quad (A17)$$

$$(x + x_0)^2 = (x - x_0)^2/r^2 \quad (A18)$$

The solution of Eq. A17 is

$$x = -x_0 \left(\frac{1-R/r^2}{1+R/r^2} \right) \quad (A19)$$

Substituting Eq. A19 into Eq. A17, we obtain:

$$R = r \quad (A20)$$

From Eq. A19 it follows that

$$x = -x_0 \left(\frac{r-1}{r+1} \right) \quad (A21)$$

For symmetrical doublets ($R = r = 1$), $x = 0$. If $r > 1$, then $x < 0$, i. e., the zero point may correspond to the first doublet peak. In this case, relative shift

$$\xi_1 = 0.5\{1 - (r - 1)/(r + 1)\} \quad (A22)$$

does not depend on the separation of the doublet peaks. For example, if $r = 2$ and 3, then $\xi_1 = -1/3$ and 0.25, respectively. For $= 1/r$, Eq. A21 only changes its sign ($x > 0$). Therefore, the zero point may correspond to the second doublet peak and/which leads to $\xi_2 = -\xi_1$.

References

- [1] B. K. Sharma, Spectroscopy. 19th Ed. India, Meerut-Delhy: Goel Publishing House, 2007.
- [2] L. Smeller, "How precise are the positions of computer-determined peaks?", Appl. Spectr., 1998, vol. 52, pp. 1623-1626.
- [3] H. Witjes, M. Pepers, W.J. Melssen and L.M.C. Buydens, "Modelling phase shifts, peak shifts and peak width variations in spectral data sets: its value in multivariate data analysis", Anal. Chim. Acta, 2001, vol. 432, pp. 113-124.
- [4] Soo Ryeon Ryu, Isao Noda and Young Mee Jung, "What is the origin of the positional fluctuation of spectral features: true frequency shift or relative intensity changes of two overlapped bands?", Appl. Spectr., 2010, vol. 64, pp. 1017-1021.
- [5] T. O'Haver, Fourier Deconvolution, <http://terpconnect.umd.edu/~toh/spectrum/Deconvolution.html>.
- [6] J. M. Dubrovkin and V. G. Belikov, Derivative Spectroscopy. Theory, Technics, Application. Russia: Rostov University, 1988.
- [7] G. Talsky. Derivative Spectrophotometry. Low and Higher Order. Germany, Weinheim: VCH Verlagsgesellschaft, 1994.
- [8] J. J. Olivero and R.L. Longbothum, "Empirical fits to the Voigt line width: A brief review", J. Quant. Spectroscopy and Radiative Transfer, vol. 17, 1977, pp. 233-236.
- [9] V. A. Lóenz-Fonfría and E. Padrós, "Method for the estimation of the mean lorentzian bandwidth in spectra composed of an unknown number of highly overlapped bands", Appl. Spectr., 2008, vol. 62, pp. 689-700.
- [10] L. I. Turchak and P. V. Plotnikov, Fundamentals of numerical methods, Russia, Moscow: Fizmatlit, 2003.
- [11] C. Lanczos, Applied analysis, New York: Dover Publication, Inc, 1988.