



Evaluation of the Peak Location Uncertainty in Spectra. Case Study: Exponentially Modified Asymmetrical Gaussian Doublets

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Abstract: The dependences of the relative peak shifts of the exponentially modified asymmetrical Gaussian doublets on the peak separation were evaluated numerically in a wide range of varied parameters of doublet lines. The "wing effect" of asymmetrical lines on the relative peak shifts was discussed. Qualitative shift patterns were obtained.

Keywords: modified asymmetrical Gaussian doublets; peak identification; peak location uncertainty; spectral line profiles.

I. Introduction

Location of the spectral peaks (line and bands) is the most important quantitative parameters widely employed in theoretical and applied spectroscopy [1]. For example, classical methods of identifying unknown elements and chemical compounds are usually based on comparing the experimentally measured peak positions with those found in the spectral libraries. However, overlapping of adjacent spectral contours and uncorrected background often cause apparent peak shifts, which lead to errors in spectral interpretation and establishing relationships between peak position and physicochemical properties of the sample under study. Broadening of the elementary spectral components and disturbing their symmetry due to the intra- and inter-atomic and molecular interactions produce additional problems. In this connection, a priori evaluation of the uncertainty in peak location measurements using synthesized overlapping components is very important. These models should be build using superposition of the spectral components of known form (e.g., Gaussian, Lorentzian and Voigt) which parameters are varied over a wide range of values. Comparison of experimentally observed and calculated peak shifts allows distinguishing between the apparent and the true shifts.

Evaluation of the peak location uncertainty in spectra, in the second-order derivative spectra and in Tikhonov deconvoluted spectra which are consisted of symmetrical lines of different shapes, has been performed in our previous papers [2-4]. The goal of the present study was error evaluation in determining peak positions of overlapping asymmetrical lines. Asymmetrical line shapes have been approximated by numerous mathematical functions [5]. We chose new version of the exponentially modified Gaussian peak which parameters allowed us to control the line asymmetry in a flexible manner [6].

In what follows, for the sake of simplicity, term "line" is used instead of term "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. Model

Consider the 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 exponentially modified Gaussian line (EMGL) was studied in this work. If position of the Gaussian line maximum is zero then EMGL can be represented as the sum of symmetrical and asymmetrical parts [7]:

$$F(x) = (F^{sym}(x))^+ + (F^{asym}(x))^+, \quad (2)$$

where

$$(F^{sym}(x))^+ = 2 \int_0^\infty \frac{\tilde{F}(\omega) \cos(\omega x)}{1 + \tau^2 \omega^2} d\omega, \quad (3)$$

$$(F^{asym}(x))^+ = 2\tau \int_0^\infty \frac{\tilde{F}(\omega) \sin(\omega x)}{1 + \tau^2 \omega^2} \omega d\omega \quad (4)$$

$$\tilde{F}(p) = w \sqrt{\pi}/\beta_G \exp(-p^2/4\beta_G^2), \quad (5)$$

tilde is the sign of Fourier transform (FT), ω is the angular frequency, τ is the asymmetry parameter, $p = w\omega$, and $\beta_G = 2\sqrt{\ln 2}$. For simplicity the line intensity is taken as unity.

According to Eqs. 3 and 4 Eq. 2 is the weighted sum of symmetrical part and its derivative:

$$F(x) = (F^{sym}(x))^+ - \tau d(F^{sym}(x))^+ / dx \quad (6)$$

New version of the integrand (3) for $w = 1$ is [6]:

$$(\sqrt{\pi}/\beta_G) \exp(-\omega^2/4\beta_G^2)/(1 + \tau^2\omega^2)^n, \quad (7)$$

where $n \geq 1$ may be a fraction.

If the maximum of Gaussian line is located in the point x_0 then the correcting multiplier of Eq. 7 is equal to

$$C = \exp(-jx_0\omega), \quad (8)$$

where $j = \sqrt{-1}$.

We studied lines which have right asymmetry ($\tau > 0$).

It was found [6] that for $\tau < 0.2$ $x_m \cong \tau$ and does not depend on n . For $\tau > 0.2$ $x_m(\tau) < \tau$; x_m slightly increases with increasing n .

EMGL line is broadened if τ and n increase (Fig. 1); the right half-width becomes wider than the left half-width (Fig. 1c).

b. Relative shift

The relative shift of the line position is usually measured relative to the line width. However, in practice, the widths can be evaluated very approximately because the lines are overlapping [8, 9]. Therefore, we chose to calculate the shifts with respect to the separation of the doublet components, which estimation can be readily obtained visually. In this case, the relative shift of the resolved doublet peak for the i^{th} component has the form:

$$\xi_i = (x_{mi}^d - x_{mi}^s - (-1)^i x_0) / 2x_0, \quad (9)$$

where $i = 1, 2$, x_{mi}^d and x_{mi}^s are the measured points of i^{th} -peak maximum of the doublet and of the isolated peak, respectively. The term x_{mi}^s eliminates peak shifts which appear due to the dependence of the peak maximum position on τ and n . Thus ξ_i depends only on the degree of the doublet line overlap.

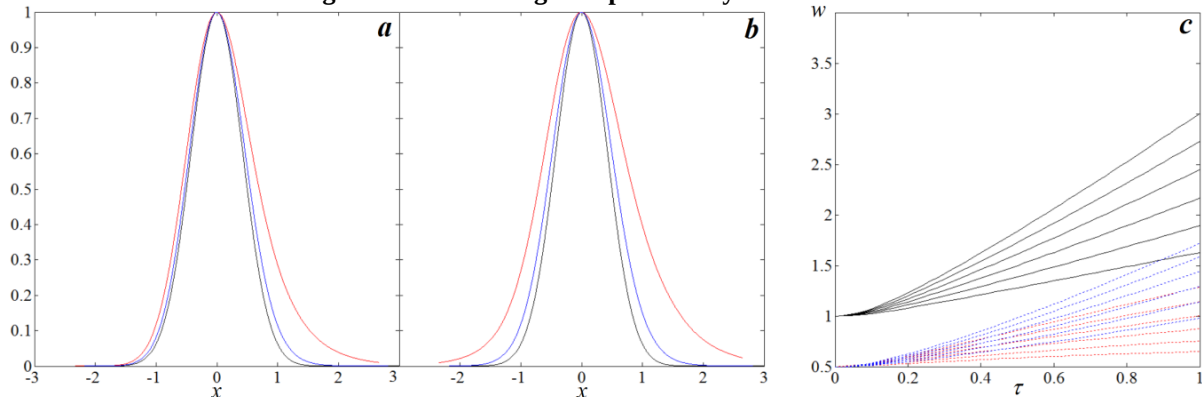
The minimum calculation errors of x_{mi} depend on the sampling interval (h) of spectra along x-axis [10]. E. g., for $h = 0.002$ and $x_0 = 0.4$ minimum absolute value of the uncertainty of ξ_i : $\min \Delta \xi_i \leq 100h/(2x_0) = 0.25\%$. The uncertainty decreases for the smaller sampling interval. However, it is unpractical to further decrease the h -value since the number of the spectral points will be very large. It was shown that the measurement error of the peak maximum location may be made smaller than the sampling interval using polynomial approximation of the spectrum which signal-to-noise ratio is high [10]. Therefore the spectral curve in the vicinity of the peak maximum was approximated by the 3rd-order polynomial. Number and location of the polynomial points were selected according to the best-fit criterion. The first derivative of this polynomial is equal to zero in the point x_{mi} .

II. Results of Computer Modelling and Discussion

a. Noise impact on peak shifts

Random normal noise with zero mean was added to the doublet spectrum. Noisy spectrum has been smoothed using multiply three-point moving average filter. Obtained results (Fig. 2a) show that the smoothing slightly reduces doublet resolution for $\tau = 0.5$ and increases peak shifts. However, the noise impact is not significant even for the noise standard deviation $\eta = 0.02$ (signal-to-noise ratio is less than 50).

Figure 1. Broadening of exponentially modified Gaussian lines



(a, b) $\tau = 0, 0.2$ and 0.5 (black, blue and red curves, respectively); peaks are shifted to $x_m = 0$. $n=1$ (a), $n=1.5$ (b). (c) Full line width, left half-width and right-half width (black, blue and red curves, respectively). $n=1, 1.2, \dots, 2$ from the bottom to the top plots, respectively.

b. Equal-width lines ($\tau=1$)

1. The dependences of the relative shifts on x_0 ($\xi(x_0)$) are represented in Figs. 2, 4 and 5. Projections of the plots $\xi(x_0)$ (Figs. 2a and b) onto the y-axis (dependence $\xi(\tau)$) are given in Fig. 3. The rule of symmetry [2]:

$$\xi_1^{(r=1)}(R, x_0) = -\xi_2^{(r=1)}(1/R, x_0) \quad (10)$$

is valid only for symmetrical lines. If τ and n increase then doublet resolution significantly decreases, and for a given x_0 the shifts increase. With increasing x_0 the long right wing of the 1st line of asymmetrical doublets overlaps the 2nd line (*the wing effect*). Therefore the maximum of the 2nd line is shifted more than the maximum of the 1st line. The wing effect is most pronounced when $\tau = 0.5$ and $n = 1.5$ (Figs. 2d and 3b).

2. Although the more intense 2nd line (larger R values) causes larger shifts of the 1st line, its own shifts decrease (Figs. 4 and 5, plot a-c). Thus, if $R_1 > R_2$, then

$$|\xi_1^{(r=1)}(R_1, x_0)| > |\xi_1^{(r=1)}(R_2, x_0)|, |\xi_2^{(r=1)}(R_1, x_0)| < |\xi_2^{(r=1)}(R_2, x_0)| \quad (11)$$

Asymmetrical wings have significant impact on the measured position of the maximum of the weak 2nd line ($R < 1$) (Figs. 4 and 5, plots d-f).

3. Dependences $\xi(x_0)$ rapidly increase near resolution limit.

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

1. As pointed out above, with increasing τ and n resolution of doublet lines worsens due to the line broadening [6]. The maximum of the 2nd line is shifted to the right wing of the 1st line which is very long for $r > 1$. This wing decays more slowly than the pure Gaussian line; therefore, the relative shifts of the 2nd line increase as compared with those of symmetrical lines (*the wing effect*) (Figs. 6-17).

2. If $R = 1$ and $\tau = 0.2$ then the shifts of the wide 2nd line ($r = 2$ and 3) are less than those of the 1st line. However, for strongly asymmetrical lines ($\tau = 0.5$) $|\xi_2| > |\xi_1|$ (Figs. 6 and 9).

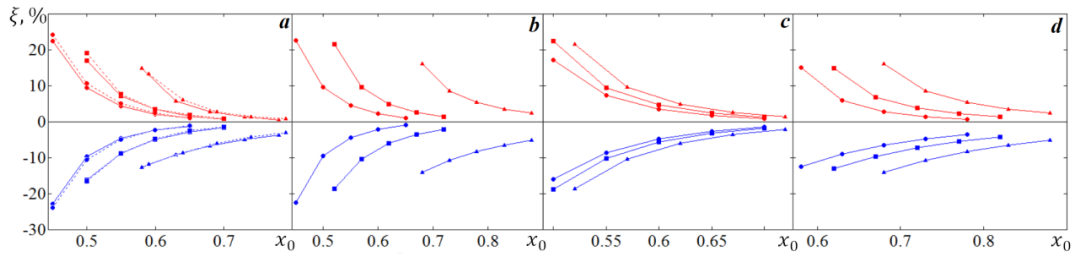
3. The shifts of the intense ($R > 1$) and wide 2nd line ($r = 2$ and 3) is significantly less than of the 1st line (Figs. 7, 8, 10 and 11, plots a-c). There are exceptions near resolution limit ($R = 2, r = 3$) (Figs. 10a and 11a) [2].

4. The shifts of the 1st intense line overlapped by wide weak line are significantly less than those of the 2nd line for $\tau = 0.5$ (Figs. 7, 8, 10 and 11, plots d-f).

5. For $R = 1$ the shifts of the narrow 2nd line ($r = 0.5$ and $1/3$) are larger than those of the 1st line (Figs. 12 and 15). Some exceptions are seen near resolution limit. For $R > 1, r = 0.2$ and $1/3$ $|\xi_2|$ and ξ_1 are less than 4% (Figs. 13 and 16, plots a-c).

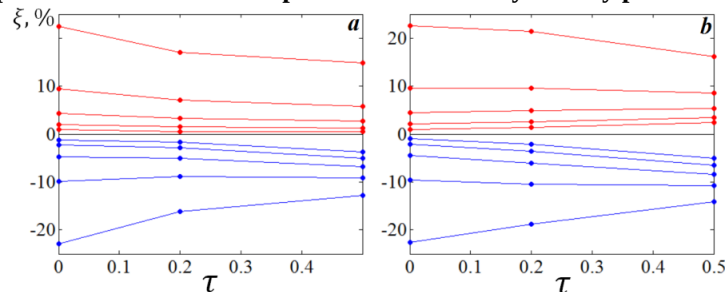
6. The shifts of the 1st line overlapped by narrow weak 2nd line are significantly less than those of the last line (Figs. 13, 14, 16 and 17, plots d-f).

Figure 2. Dependences of the relative peak shifts on the line separation ($R = 1, r = 1$)



1st line - red curves, 2nd line - blue curves. $n=1$ (a) and 1.5 (b), $\tau = 0$ (●), 0.2(■), 0.5(▲) $\eta = 0$ (—) and 0.02 (···). $\tau = 0.2$ (c) and 0.5 (d), $n = 1$, (●), 1.2(■), 1.5(▲).

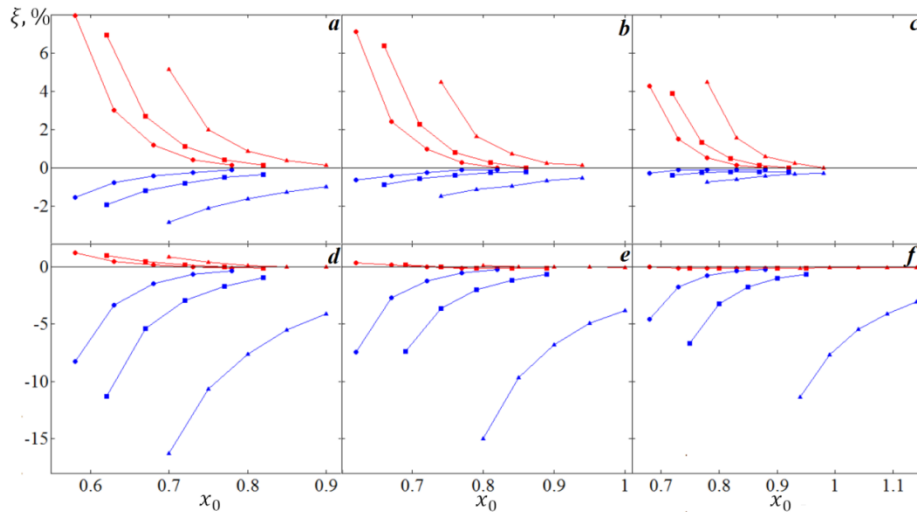
Figure 3. Dependences of the relative peak shifts on the asymmetry parameter ($R = 1, r = 1$)



1st line - red curves, 2nd line - blue curves. $n=1$ (a) and 1.5 (b). x_0 values are given in the table from the top to the bottom plots for the 1st line and vice versa for the 2nd line.

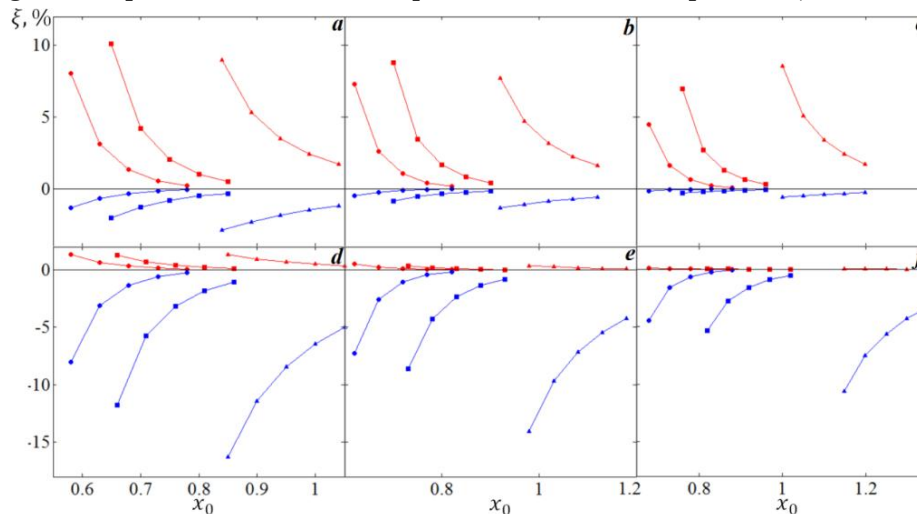
τ	$n=1$	$n=1.5$
0	0.45 0.50 0.55 0.60 0.65	0.45 0.50 0.55 0.60 0.65
0.2	0.50 0.55 0.60 0.65 0.70	0.52 0.57 0.62 0.67 0.72
0.5	0.58 0.63 0.68 0.73 0.78	0.68 0.73 0.78 0.83 0.88

Figure 4. Dependences of the relative peak shifts on the line separation ($n = 1, r = 1$)



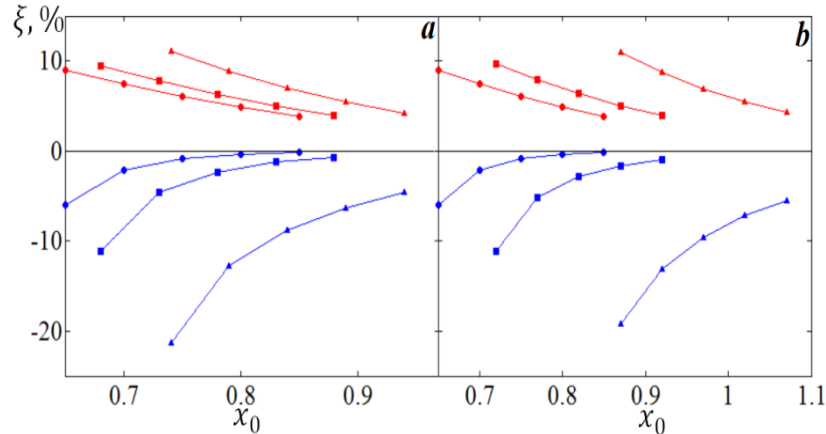
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 5. Dependences of the relative peak shifts on the line separation ($n = 1.5, r = 1$)



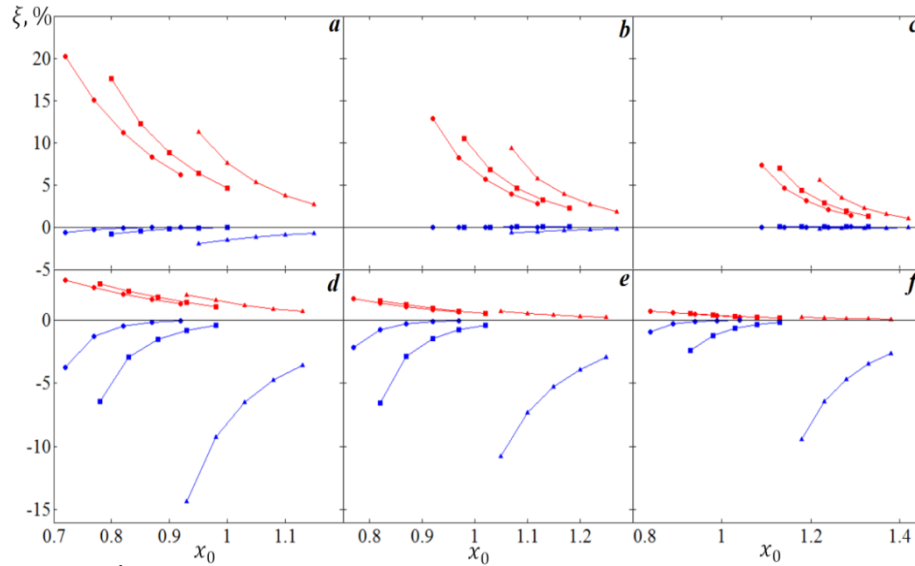
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 6. Dependences of the relative peak shifts on the line separation ($R = 1, r = 2$)



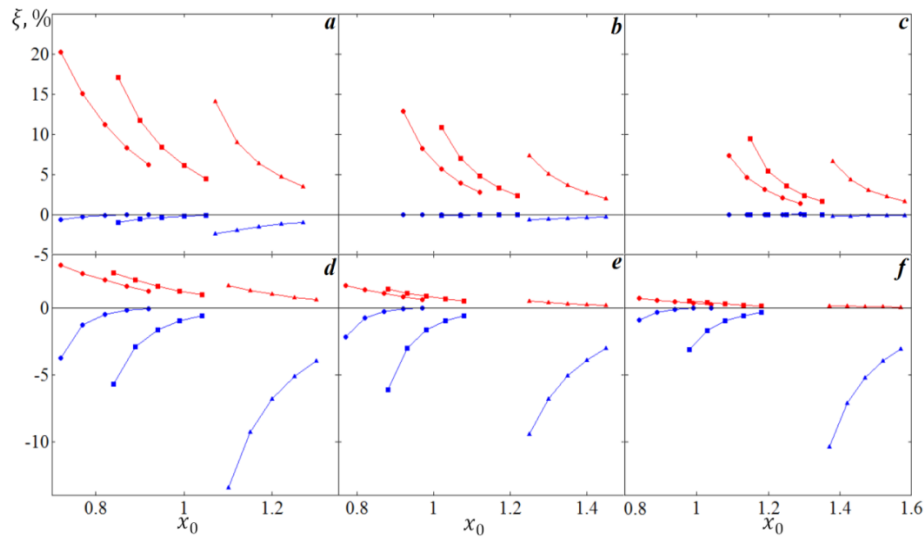
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $n=1$ (a) and 1.5 (b).

Figure 7. Dependences of the relative peak shifts on the line separation ($n = 1, r = 2$)



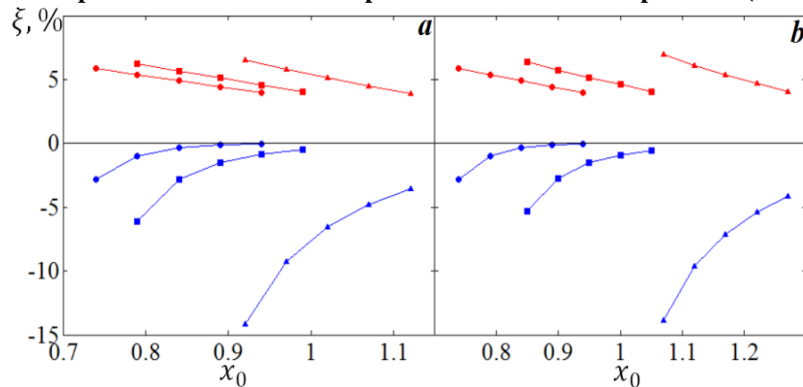
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 8. Dependences of the relative peak shifts on the line separation ($n = 1.5, r = 2$)



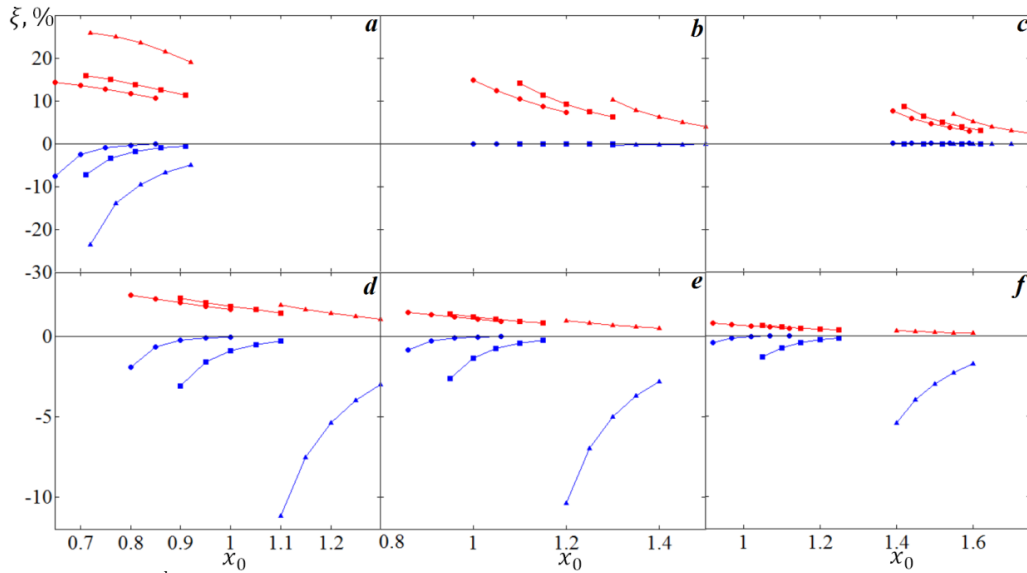
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 9. Dependences of the relative peak shifts on the line separation ($R = 1, r = 3$)



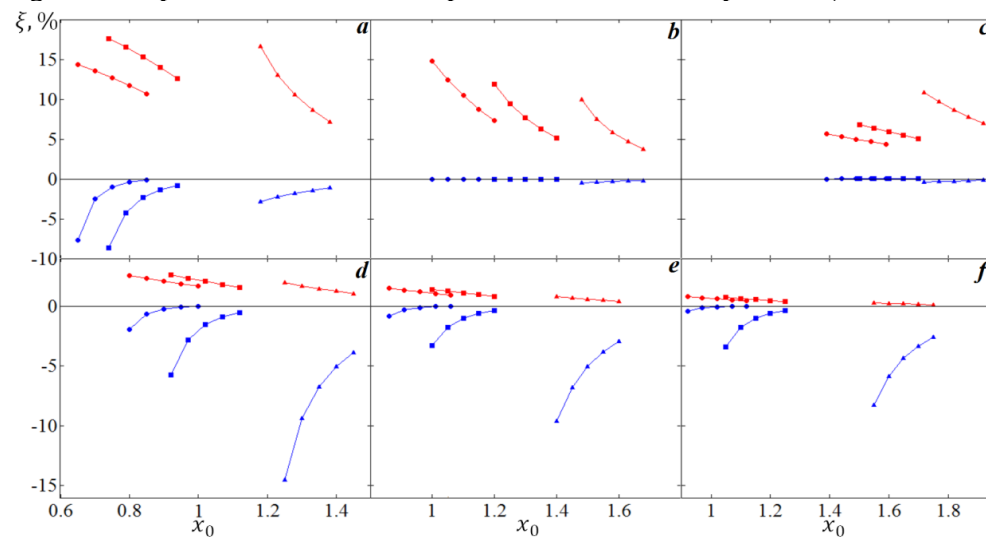
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $n=1$ (a) and 1.5 (b).

Figure 10. Dependences of the relative peak shifts on the line separation ($n = 1, r = 3$)



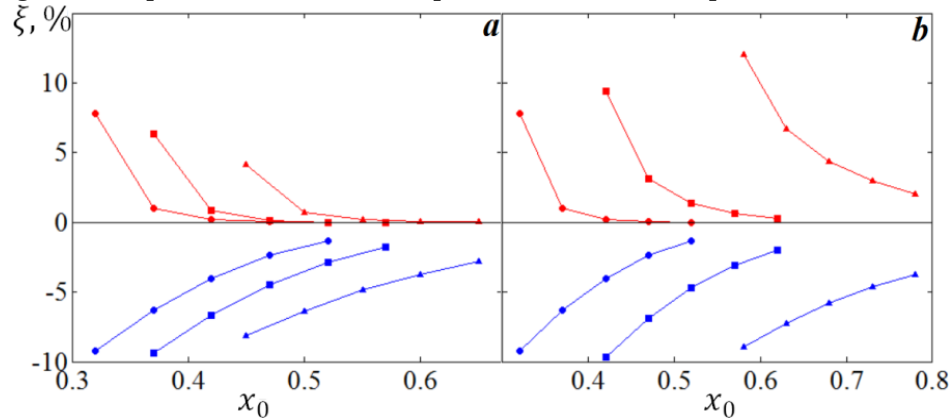
1st line - red curves, 2nd line - blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 11. Dependences of the relative peak shifts on the line separation ($n = 1.5, r = 3$)



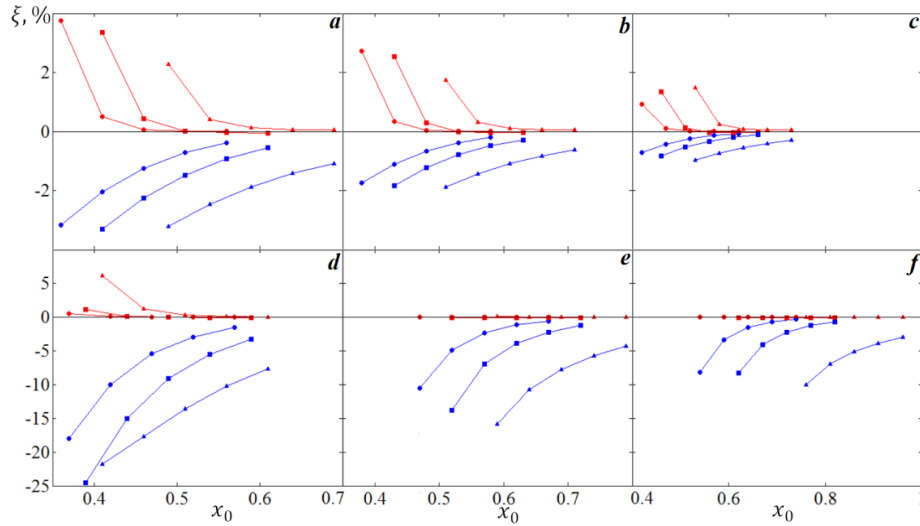
1st line - red curves, 2nd line - blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 12. Dependences of the relative peak shifts on the line separation ($R = 1, r = 0.5$)



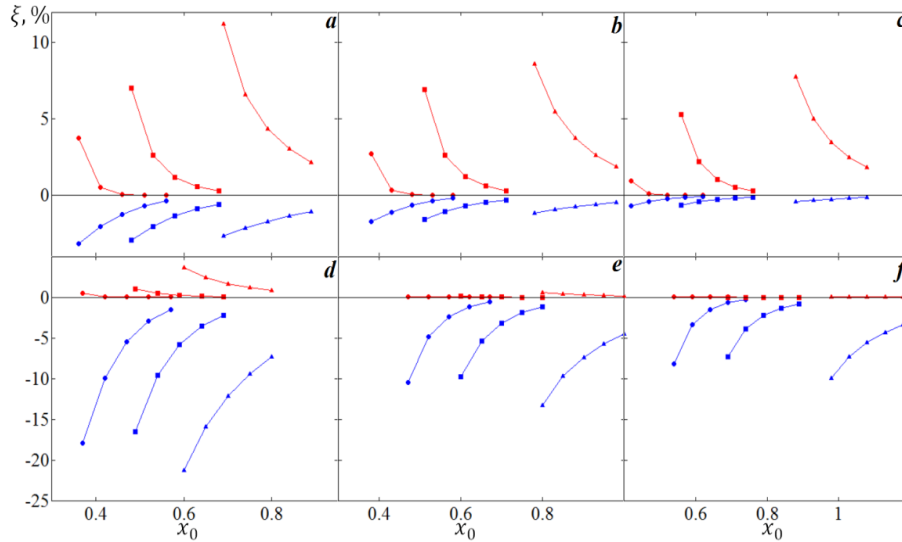
1st line - red curves, 2nd line - blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $n=1$ (a) and 1.5 (b).

Figure 13. Dependences of the relative peak shifts on the line separation ($n = 1, r = 0.5$)



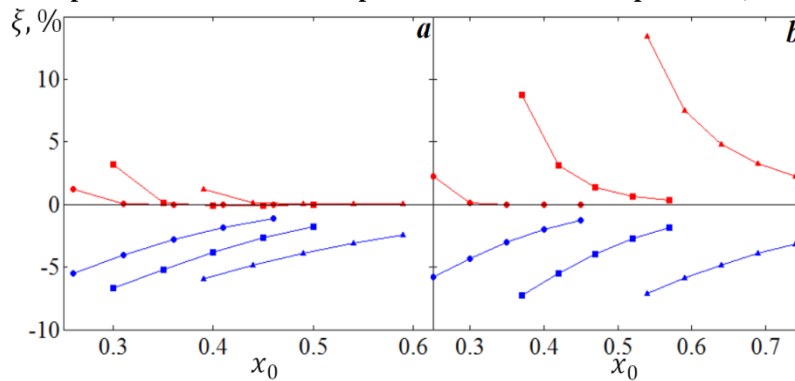
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 14. Dependences of the relative peak shifts on the line separation ($n = 1.5, r = 0.5$)



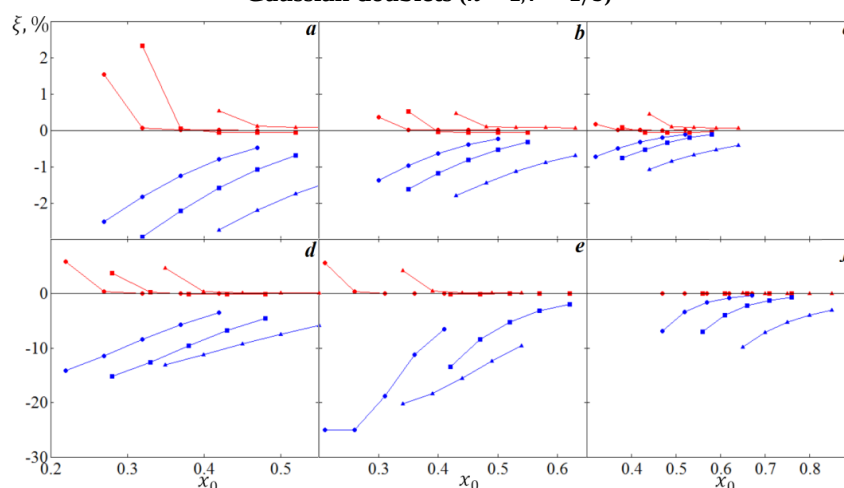
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 15. Dependences of the relative peak shifts on the line separation ($R = 1, r = 1/3$)



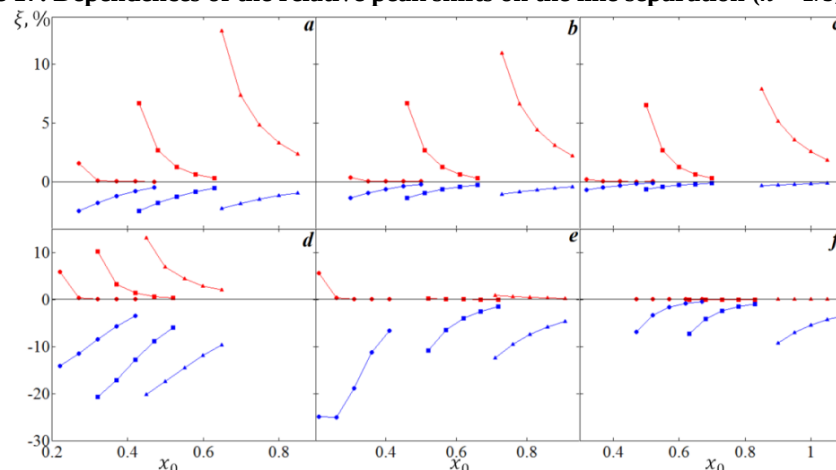
1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $n=1$ (a) and 1.5 (b).

Figure 16. Dependences of the relative peak shifts on the line separation of the modified asymmetrical Gaussian doublets ($n = 1, r = 1/3$)



1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

Figure 17. Dependences of the relative peak shifts on the line separation ($n = 1.5, r = 1/3$)



1st line - red curves, 2nd line – blue curves. $\tau = 0$ (●), 0.2 (■), 0.5 (▲), $R=2, 3, 5, 0.5, 1/3, 0.2$ for the plots a-f, respectively.

7. Obtained results showed that peak asymmetry results in additional increase in peak shifts caused by peak overlap. These shifts must be taken into account in performing spectrochemical analysis. E. g., the measured position of the asymmetrical peak maximum must be corrected if it is used as an initial guess for decomposition of a complex spectral contour into its elementary components.

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