



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

www.iasir.net

Resolution Limit of Asymmetrical Doublets

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Abstract: The resolution limit of doublets that consist of symmetrical and asymmetrical lines of unequal intensities and widths was, for the first time, evaluated theoretically and numerically using the Sparrow and the information criteria. Gaussian, Lorentzian, Voigt, and sinc-squared-like line shapes were studied. The obtained results may be useful for practical applications.

Keywords: spectroscopy; resolution limit; symmetrical and asymmetrical lines; Sparrow and information criteria

I. Introduction

Spectral line parameters, such as location and intensity, are the main source of spectrochemical information. However, overlapping of the lines often hampers the precise measurement of these parameters. The cause of overlapping is the line width being non-zero because of line broadening. The minor natural line width is usually masked by Doppler and collision-induced broadening [1]. In addition, the resolving power of an optical instrument is limited by the width of its instrumental function [1]. The foregoing consideration points to the importance of evaluating the resolution limit of spectral lines.

The resolution limit of an optical instrument, which is one of the main concepts of optics and spectroscopy, is based on certain criteria [2]-[6]. The most common of these are the historically first suggested diffraction-related Rayleigh criterion [1] and the mathematical Sparrow criterion [7]. With the advent of computer technology, more elaborate mathematical criteria have been developed to estimate the resolution limit, e.g., the relative depth of the dip in the center of a symmetrical doublet [8], the absolute value of the minimum in the Fourier spectrum of this doublet [9], and the information measure of the distinctiveness between two spectra [10]. However, the comparative studies of the above methods were conducted only for symmetrical doublets [3], [11].

The goal of this research was extending the studies of the resolution problem to the case of doublets that consist of symmetrical and asymmetrical lines of unequal intensities and widths. These doublets are the characteristic structural elements of spectral profiles.

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

II. Theory

A. Models

Consider doublet (Fig. 1a)

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

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 [12]

$$F_G(x) = \exp(-x^2/(1 - \tau x)^2), \quad (2)$$

where $\beta_G = 2\sqrt{\ln 2}$ and τ is the line asymmetry parameter.

b. Lorentzian function [13]

$$F_L(x) = \exp(\tau(1 - \tan^{-1}x))/(1 + x^2), \quad (3)$$

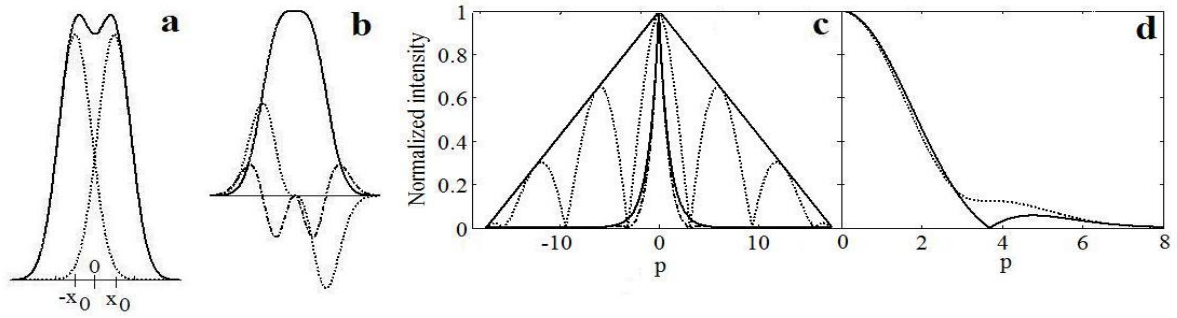
where $\beta_L = 2$;

c. Voigt function (consisting only of symmetrical components: $\tau = 0$) [14]

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

where $t_G = w/w_G$ and $t_L = w/w_L$.

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Figure 1 Doublets and their Fourier transforms

Gaussian doublets ($R = r = 1$) and their derivatives: (a) $\delta = 1$, (b) $\delta = 0.8494$, $D(-)$, $D^{(1)}(\dots)$, $D^{(2)}(-)$. Fourier images: (c) $\tilde{s}_1(-)$, $\tilde{s}_2$ of Lorentzian($- \cdot -$), and sinc-squared($\dots$) doublets ($R = r = 1, \delta = 1$). (d) doublet “b” ($-$) and Gaussian doublet ($\dots$) ($R = 0.5, r = 1, \delta = 1$).

The width of the Voigt profile [14] is

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

d. Sinc-squared function [3]:

$$F_S(x) = \text{sinc}^2(x), \quad (6)$$

where $\text{sinc}(x) = \sin(x)/x$ and $\beta_S = 2.7831$.

B. Resolution criteria

According to the Sparrow resolution limit (δ_{SP}) [7], the separation of the doublet lines is minimal when the derivatives in the center of the doublet (1) equal to zero (Fig. 1b):

$$D^{(1)}(0) = D^{(2)}(0) = 0. \quad (7)$$

The mathematical expressions for the derivatives of the typical lines are given in Appendix A.

The information measure to distinguish between spectra s_1 and s_2 has the form [10]:

$$\mu(s_1, s_2) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{|\tilde{s}_1 - \tilde{s}_2|^2}{G(\omega)} d\omega, \quad (8)$$

where the tilde character is the symbol of Fourier transform, G is the spectral noise power, and ω is the angular frequency.

The probability that two spectra can be distinguished from one another equals

$$P(\mu) = 0.5 + \Phi(\sqrt{\mu/8}), \quad (9)$$

where $\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_0^z e^{-t^2/2} dt$ is the cumulative distribution function of the standard normal distribution.

For the white noise $G(\omega) = \pi\sigma^2/\omega_0$, where σ^2 is the noise variance, $[-\omega_0, \omega_0]$ is the angular frequency range.

Let us introduce the following notations of the Fourier transform of the doublet

(a) with coinciding maxima:

$$\tilde{s}_1 = \tilde{F}_1 + \tilde{F}_2, \quad (10)$$

(b) with maxima separated by Δ :

$$\tilde{s}_2 = \tilde{F}_1 \exp(-jp\delta/2) + \tilde{F}_2 \exp(jp\delta/2), \quad (11)$$

where $j = \sqrt{-1}$ and $p = \omega w$.

It can be shown that

$$\tilde{F}_1 = Cw\theta(p), \quad (12)$$

$$\tilde{F}_2 = CwRr\theta(rp), \quad (13)$$

where C and θ are given in Table 1 for symmetrical lines. For these lines, $\theta(p)$ is a real function, while for asymmetrical lines, it is a complex function. From (8) and (10)-(13), it follows that

$$\mu(s_1, s_2) = 2(p_0/\pi^2\sigma^2) \Psi(\delta, R, r), \quad (14)$$

where

$$\Psi(\delta, R, r) = C^2 \int_{-\infty}^{+\infty} \sin^2(p\delta/4) \chi(\delta, R, r) dp, \quad (15)$$

$$\chi(\delta, R, r) = |\theta(p)|^2 + R^2 r^2 |\theta(rp)|^2 - 2Rr[C \cos(p\delta/2) + S \sin(p\delta/2)], \quad (16)$$

$C = \theta_{Re}(p)\theta_{Re}(rp) + \theta_{Im}(p)\theta_{Im}(rp)$; $S = \theta_{Re}(p)\theta_{Im}(rp) - \theta_{Im}(p)\theta_{Re}(rp)$; Re and Im denote the real and the imaginary part, respectively.

Analytical calculations of Eq. 15 were performed only for symmetrical Gaussians and Lorentzians (Appendix B). For asymmetrical Gaussian, Lorentzian, Voigt, and sinc-squared lines, only numerical calculation was performed because analytical integration (15) appeared to be very complicated.

Table 1 Parameters of Fourier transforms for symmetrical lines

Line	C	$\theta(p)$
Gaussian	$\sqrt{\pi}/\beta_G$	$\exp(-p^2/4\beta_G^2)$
Lorentzian	π/β_L	$\exp(- p /\beta_L)$
Voigt	$t_G t_L \beta_G \beta_L$	$\exp(-(p^2/4t_G^2\beta_G^2))$
$\text{sinc}^2(p)$	$1/(\sqrt{2\pi}\beta_S)$	$\text{tri}(p/(2\pi\beta_S))$

tri is the triangle function: $\text{tri}(t/b) = \begin{cases} 1 - |t/b|, & t < |b| \\ 0, & \text{otherwise} \end{cases}$

Since the resolution limits (δ_{lim}) of different doublets should be compared under similar conditions (i.e., information measure μ should be the same), the value of δ_{lim} for a particular doublet was obtained from the expression

$$\Psi(\delta_{lim}, R, r) = \Psi(\delta_{SP}, R = 1, r = 1), \quad (17)$$

where δ_{SP} is the Sparrow resolution limit of the doublet.

Consider two anti-symmetrical doublets that are composed of equal-width components ($r = 1$) with relative intensities $R_1 = 2$ and $R_2 = 1/R_1 = 0.5$ of the second component (Figs. 2a-I and 2a-II, respectively). The second doublet can be obtained from the first one by dividing its intensities by 2 (Fig. 2a-III) and inverting. According to (17), the informational measure μ (8) calculated for doublets must be the same. This condition can be fulfilled if $\chi(\delta, R, r)$ (16) is divided by R^2 for $R > 1$ and for any r . Then for $r = 1$, doublets “I” and “II” coincide. However, in the general case ($r \neq 1$), after the division procedure and inverting, anti-symmetrical doublets do not coincide for $R < 1$ and $R > 1$ (Fig. 2b-III) and μ -values are also different.

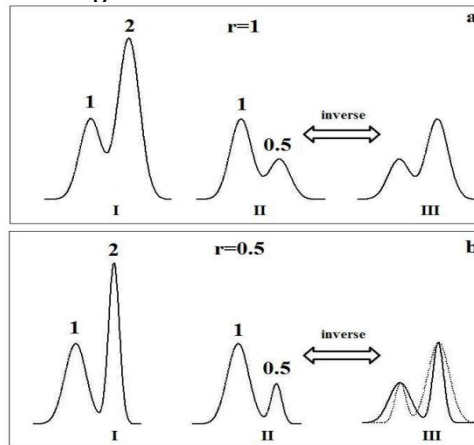
It should be emphasized that the resolution limits of doublets belonging to the same group were compared using the Sparrow and the information criteria separately.

Because of the high-intensity lobes of the sinc-squared function (6) (Fig. 1c), Eq. (17) has no reasonable solution. Therefore, the information measure for this function was not calculated.

According to the Petrash resolution criterion [9], the second lobe amplitude in the modulus of the Fourier spectrum of a doublet equals to the resolution measure. Thus the resolution measure can be obtained from the modulus of the doublet Fourier image (11) as:

$$|\tilde{s}_\delta(p, \delta)| = Cw[\theta^2(p) + R^2 r^2 \theta^2(rp) + 2Rr\theta(p)\theta(rp)\cos(\delta p)]^{1/2}. \quad (18)$$

Function (18) has a local maximum (corresponding to the second lobe) at p_{max} , which is located next to the global maximum at $p = 0$. From the plots of normalized values $|\tilde{s}_\delta(p, \delta)|/|\tilde{s}_\delta(0, \delta)|$ vs p (Fig. 1d), it can be seen that the first and the second lobes of the Fourier transform of an asymmetrical doublet strongly overlap

Figure 2 Inversion of doublets

although the separation of the doublet lines is larger than the Sparrow limit. In this case, it is impossible to measure the second lobe amplitude and this criterion appears to be of no practical use for asymmetrical doublets.

III. Results and Discussion

A. Doublets consisting of equal-width components

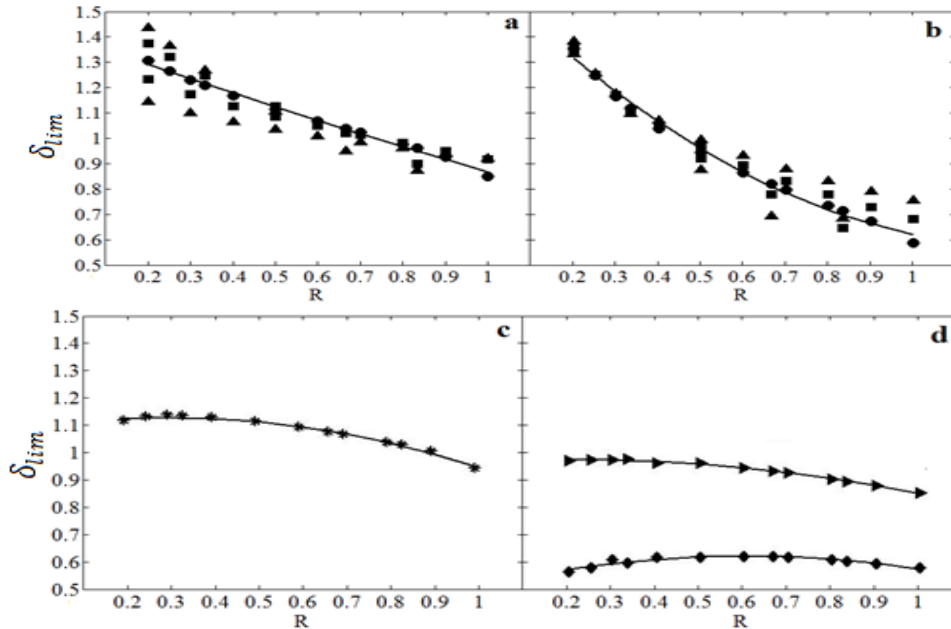
It was pointed out above that doublets with the relative line intensities R and $1/R$ have the same resolution limit δ_{lim} . Therefore, dependences $\delta_{SP}(R)$ and $\delta_{inf}(R)$ are defined in the range of $(0, 1]$ (Fig. 3). It can be seen from Figs. 3a-c that the Sparrow resolution limit decreases (the resolution increases) when the relative intensity of the

second component increases. In contrast to this, the information resolution limit δ_{inf} , decreases with R only slightly for Gaussians, while in the case of Lorentzians it has a convex form (Fig. 3d). The difference between the $\delta_{SP}(R)$ and $\delta_{inf}(R)$ behavior is explained by the fact that the first criterion takes into account only the central peak region, while in the second one the whole spectrum, including the wings, is considered. Figure 3a shows that the small line asymmetry of the Gaussians improves resolution, while the impact of the Lorentzian line asymmetry is opposite (Fig. 3b).

B. Doublets consisting of non-equal-width components

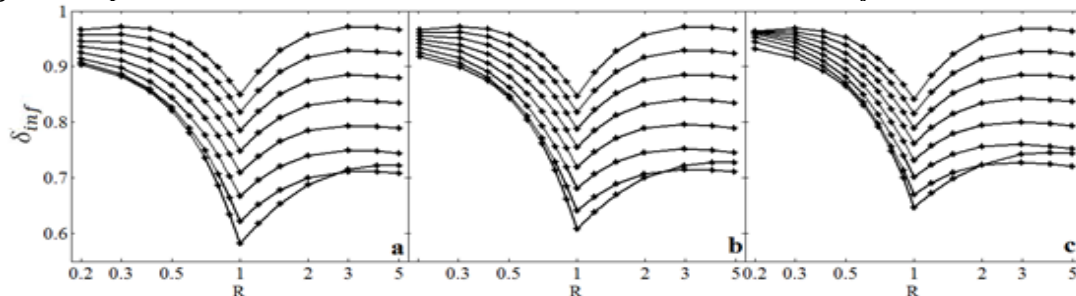
In contrast to the constant location of the information resolution minimum, δ_{inf}^{min} , at $R = 1$ (Figs. 4a, 5a), dependence $\delta_{SP}(R)$ reaches its minimum, δ_{SP}^{min} (corresponding to the best resolution), when $R \approx r$ (Fig. 6a). The exception is the Gaussian doublet with $r = 0.3$, where $\delta_{SP}^{min} = 0.3277$ is located in the neighbourhood of $R = 0.19$ (Figs. 6a, 7b). We have found that the location of the doublet shoulder changes from the left to middle and then to the right position when function $\delta_{SP}(R)$ passes the point of its minimum (δ_{SP}^{min}) (Fig. 7). Moreover, it can be seen from Fig. 6a that the transition to the left wing causes a steep increase of this function when $r < 1$. This effect is very strong in the case of $r = 0.3$ (Figs. 7c, 7d).

Figure 3 Resolution limit dependences for equal-width doublets

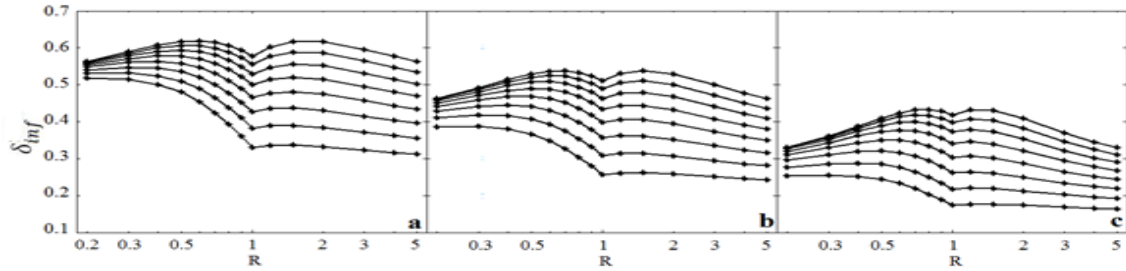


$\delta_{SP}(R)$ for (a) Gaussians ($\tau = 0$ (●), 0.0519 (■), and 0.1142 (▲)), (b) Lorentzians ($\tau = 0$ (●), 0.2 (■), and 0.5 (▲)), and (c) sinc-squared shapes. (d) $\delta_{inf}(R)$ for Gaussians (►) and Lorentzians (◆).

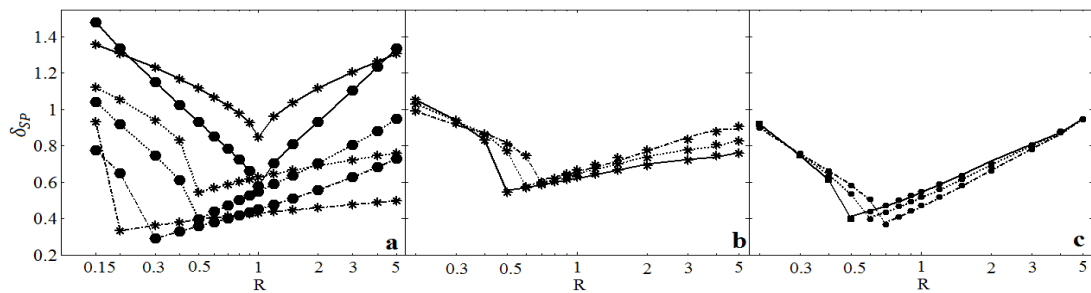
Figure 4 Dependences of the informational resolution limit on relative intensity for Gaussian doublets



$\tau = 0$ (a), 0.0519 (b), and 0.1142 (c). For the curves from top to bottom: $r = 1, 0.9, \dots, 0.3$.

Figure 5 Dependences of the informational resolution limit on relative intensity for Lorentzian doublets

$\tau = 0$ (a), 0.2 (b), and 0.5 (c). For the curves from top to bottom: $r=1, 0.9, \dots, 0.3$.

Figure 6 Dependences of the Sparrow resolution limit on relative intensity for Gaussian and Lorentzian doublets

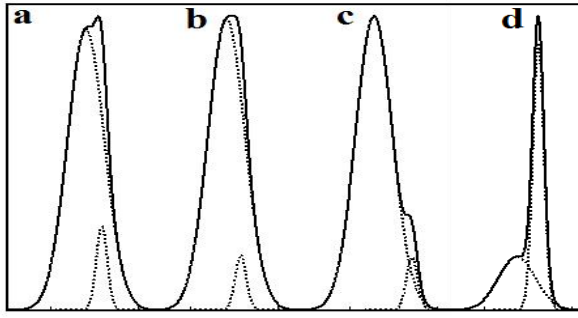
Gaussian (*) and Lorentzian (•) doublets: (a) $\tau = 0$, $r = 1$ (—), 0.5 (···), and 0.3 (— · —); (b) $r = 0.5$, $\tau = 0$ (—), 0.0519 (···), and 0.1142 (— · —); (c) $r = 0.5$, $\tau = 0$ (—), 0.2 (···), and 0.5 (— · —).

According to the Sparrow criterion, the weak narrow line that overlaps with the strong wide line (Figs. 7a, 7b) may be resolved for smaller separation than the weak wide line in the background of the strong narrow line (Fig. 7d). However, this is not always the case, as can be seen in Fig. 7c. The data presented in Table 2 and in Figs. 4a and 5a show that the information criterion $\delta_{inf}(R) < \delta_{inf}(1/R)$ if $R > 1$ and $r \neq 1$. The observed result is explained as follows. The weak narrow line is immersed in a wide line (Fig. 7b), in contrast to the weak wide line whose left wing becomes resolved (Fig. 7d). Since this wing is taken into account by the information measure, the resolution is better in the last case.

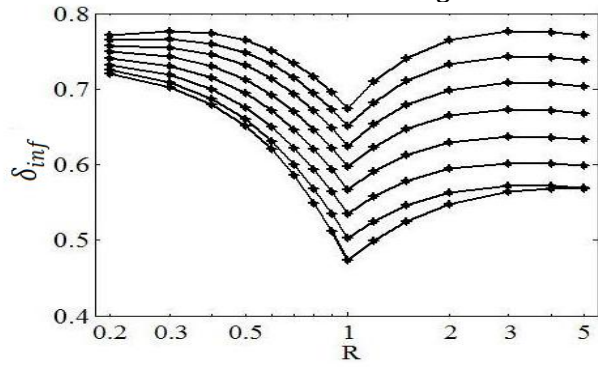
It can be seen that $\delta_{sp}^{min}(r)$ and $\delta_{inf}^{min}(r)$ are decreasing functions. The central part of dependence $\delta_{lim}(R)$ has a V-form. The wings of dependence $\delta_{sp}(R)$ are increasing functions, while the wings of dependence $\delta_{inf}(R)$ reach maximum values and then slowly decrease. The evenness of function $\delta_{inf}(R)$ relative to point $R = 1$ is impaired when $r < 1$. The Voigt profiles shown in Fig. 8 represent complex combinations of $\delta_{inf}(R)$ for Gaussian and Lorentzian lines. As a rule, small line asymmetry of Gaussians increases the δ_{sp} values, but small anomalies are observed if $R \leq 0.3$. For Lorentzians, dependence $\delta_{sp}(\tau)$ is a decreasing function in the range of $R = 5 - 0.7$. For $R \leq 0.7$, the changes of the doublet shoulder location from the left to the middle and then to the right position (Fig. 9) cause an irregular behaviour of function $\delta_{sp}(\tau)$. For Gaussians, function $\delta_{inf}(\tau)$ is an increasing one (Fig. 4), while for Lorentzians it decreases without anomalies.

Table 2 Information resolution limit for symmetrical lines

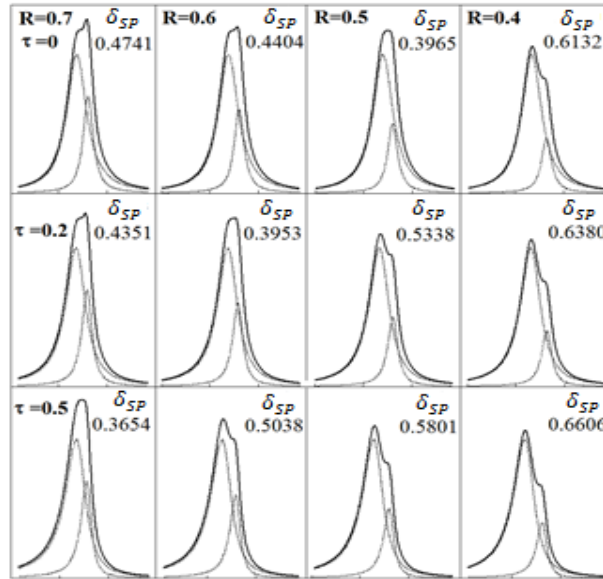
R	Gaussians		Lorentzians	
	r=0.3	r=0.5	r=0.3	r=0.5
0.2	0.9036	0.9148	0.5187	0.5403
5	0.7228	0.7448	0.3121	0.3961
0.5	0.8209	0.8443	0.4798	0.5357
2	0.6879	0.7404	0.3322	0.4313

Figure 7 Gaussian doublets

$r = 0.3$. (a) $R = 0.3$, $\delta_{SP} = 0.3632$; (b) $R = 0.19$, $\delta_{SP} = 0.3277$;
from top to bottom:
(c) $R = 0.18$, $\delta_{SP} = 0.8733$; (d) $R = 5$, $\delta_{SP} = 0.4975$.

Figure 8 Dependences of the informational resolution limit for Voigt doublets

$t_G = t_L = 0.5$. For the curves
 $r = 1, 0.9, \dots, 0.3$.

Figure 9 Anomalous behaviour of the Sparrow resolution limit for asymmetrical Lorentzian doublets

IV. Conclusion

The Sparrow criterion can be used to evaluate the visual resolution limits for overlapping spectral lines. It was pointed out above that the main drawback of this criterion is the non-smooth character of the $\delta_{SP}(R)$ dependence in the case when the two components of the doublet have non-equal widths. The Sparrow criterion can be used in practice for revealing the hidden structure of an unresolved spectrum. For this purpose, the first and the second derivatives of the spectrum are to be analysed, which is best done at high signal-to-noise ratios. The resolution can be improved by further mathematical differentiation of the spectrum [16]. However, to perform such procedure, the signal-to-noise ratio must be increased. The satellites in the derivative spectrum can also produce a false structure, which causes identification errors [16].

The information criterion can be applied to evaluating the probability of the distinctiveness between the Fourier images of two overlapping spectra. The advantage of this criterion is the smoothness of dependence $\delta_{inf}(R)$. Here, similar to the Sparrow criterion case, the distinctiveness can be improved by increasing the signal-to-noise ratio [11]. We see the perspectives of the practical application of the information criterion in the determination the reliability of the spectral curve deconvolution.

V. Appendix

A. Expressions for the derivatives of the spectral lines

For the purpose of compactness, the arguments of the functions and their derivatives are eliminated. Gaussians:

$$F_G^{(1)} = -2A_G \left(\frac{x}{B_G^2} \right) F_G, \quad (A1)$$

$$F_G^{(2)} = -2A_G \left(\frac{1}{B_x^2} \right) \left[A_G C_x F_G + \left(\frac{x}{B_x} \right) F_G^{(1)} \right], \quad (A2)$$

where $A_G = \left(\frac{\beta_G}{w} \right)$, $B_x = 1 + \tau x$, and $C_x = 1 + 2\tau x$.

Lorentzians:

$$F_L^{(1)} = A_L \left(\frac{\tau - 2x}{T} \right) F_L, \quad (A3)$$

$$F_L^{(2)} = A_L \left(\frac{\tau - 4x}{T} \right) F_L^{(1)} - 2A_L^2 \left(\frac{1}{T} \right) F_L, \quad (A4)$$

where $A_L = (\beta_L/w)$ and $T = 1 + x^2$.

Sinc-squared function:

$$F_S^{(1)} = \left. \begin{matrix} 2A_S Q_x F_S \\ 0 \end{matrix} \right\} \begin{matrix} x \neq 0 \\ x = 0 \end{matrix}, \quad (A5)$$

$$F_S^{(2)} = \left\{ \begin{matrix} 2A_S^2 \left[Q_x^2 - F_S - \frac{2Q_x \sin cx}{x} \right] \\ -1/3 \end{matrix} \right\} \begin{matrix} x \neq 0 \\ x = 0 \end{matrix}, \quad (A6)$$

where $A_S = (\beta_S/w)$ and $Q_x = (x \cos x - \sin x)/x^2$.

The limits $\lim_{x \rightarrow 0} Q_x = 0$, $\lim_{x \rightarrow 0} Q_x/x = -1/3$ were calculated by expansion by the Taylor series:

$$\sin x \approx x - x^3/6, \quad \cos x \approx 1 - x^2/2 + x^4/24.$$

The derivatives of the Voigt profile were obtained by Savitzky-Goley numerical differentiation [16].

B. Analytical expressions for Eq. (15)

Gaussians:

$$\psi_G(\delta, R, r) = k C_G^2 \left\{ 1 - Z_\delta R^2 r \left(1 - Z_\delta^{1/r^2} \right) + R r L (1 - 2Y_\delta + Y_\delta^4) \right\}, \quad (B1)$$

where $k = \beta_G \sqrt{\pi/2}$, $Z_\delta = \exp \left(-\frac{\delta^2 \beta_G^2}{8} \right)$, $L = \frac{2}{(1+r^2)}$, and $Y_\delta = Z_\delta^L$.

Lorentzians:

$$\psi_L(\delta_1, R, r) = C_L^2 \delta_1^2 \left\{ \frac{1}{1+\delta_1^2} + \frac{R^2 r}{R^2 + \delta_1^2} + \frac{2R r \delta_1^2}{M(M^2 + \delta_1^2)} \left[\frac{6\delta_1^2}{M^2 + 4\delta_1^2} - 1 \right] \right\}, \quad (B2)$$

where $\delta_1 = \delta/2$ and $M = (1+r)/2$.

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