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# DECONVOLUCION DE LINEAS ESPECTRALES EPR CON UN METODO APROXIMADO

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## RESUMEN

En este trabajo se aplica una expresión de aproximación, recientemente reportada por investigadores de este departamento, para deconvolucionar líneas espectrales Lorentziano-Gaussianas con pequeña contribución Gaussiana. La aplicación se efectúa para estudiar la línea EPR de potasio disuelto en amoníaco, línea ya reportada en diferente contexto, por otros autores. Los resultados del estudio son comparados con los que se obtienen cuando se emplea un método preciso, reportado por investigadores de este departamento.

## ABSTRACT

A recently reported approximation expression to deconvolute Lorentzian-Gaussian spectral lines, with small Gaussian contribution, is applied to study an EPR line shape. The potassium-ammonium solution line reported in the literature by other authors was used and the results are compared with those obtained by employing a precise method.

NOTE. Este trabajo se presenta en inglés debido a que fué enviado a la revista "Journal of Magnetic Resonance" para que los editores consideraran su publicación.

## INTRODUCTION

In many spectroscopies, Lorentzian lines may be affected by external and/or internal perturbations such as instrumental instabilities, thermal agitation or lattice and nuclear effects, some of which may be described by a Gaussian distribution.

In electron paramagnetic resonance spectroscopy, observed absorption lines are the result of the superposition of internal homogeneous and inhomogeneous mechanisms. Those of the first class give origin to a Lorentzian line while those of the second produce a Gaussian (1). In both cases, the resulting line is the convolution of the Lorentzian with the Gaussian and is proportional to the Voigt profile (2).

Sometimes it is of interest to know the amount of both Lorentzian and Gaussian contributions to the observed profile, so a deconvolution must be made. Since analytic integration of the Voigt profile cannot be done, people have to resort to approximation methods.

In this paper an easy-to-use approximation expression recently reported (3) is employed to deconvolute the potassium-ammonium solution EPR line (4,5). The result is compared with that obtained by using a precise method (6) which is based on a Gautschi's algorithm (7) to compute the Voigt profile. The potassium-ammonium solution line has the following characteristics

which make it adequate for this application: first, according to refs. (4,5), the recorded line is more Lorentzian than Gaussian so that the approximation expression of ref. (3), being valid for this cases, can be applied immediately; second, the line is quite isolated so that little influence from neighboring lines affects it, making the calculation easier. On the other hand, one of the lines of  $Mn^{2+}$  in a  $MgSO_4$  crystal was also studied with the cited approximation expression, however fitting was impossible as this line turned out to be more Gaussian than Lorentzian (8).

#### THE VOIGT INTEGRAL

Following Posener's notation (9), the Voigt integral may be written as:

$$H(\alpha, \nu) = \frac{\alpha}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{(\nu - y)^2 + \alpha^2} dy \quad [1]$$

In this expression, parameter  $\alpha$  is defined as:

$$\alpha = \frac{\Gamma_L}{\Gamma_G} (\ln 2)^{1/2} \quad [2]$$

where  $\Gamma_L$ ,  $\Gamma_G$  are the FWHMs of the Lorentzian and Gaussian profiles respectively;  $\nu$  is the dimensionless distance from the Voigtian line centre and is given by:

$$\nu = \nu_0 (\nu - \nu_0) (\ln 2)^{1/2} / \Gamma_0$$

where  $\nu_0$  is the frequency of the magnetic field  $h_0$  at the line centre, and where  $\Gamma_0$  is expressed in terms of the standard deviation of the Gaussian as:  $\Gamma_0 = 2 \sqrt{2 \ln 2} \sigma$ .

Integral [1] must be evaluated numerically (6,9-12); however, some authors have proposed algebraic approximations to estimate it (13-15), giving good results on particular intervals of the dimensionless parameter  $\alpha$ .

By using [1], the absorption line can be written as (8):

$$I(\alpha, \nu) = \frac{H(\alpha, \nu)}{\sqrt{2\pi} \sigma} \quad [3]$$

which can be shown to be:

$$I(\alpha, \nu) = \frac{1}{\sqrt{2\pi} \sigma} \operatorname{Re} w(iz) \quad [4]$$

where  $w(iz)$  is the complex error function and  $z = \alpha + i\nu$ . The EPR absorption line is the derivative of [3] with respect to magnetic field  $h$ :

$$\frac{\partial I(\alpha, \nu)}{\partial h} = \frac{1}{2 \sqrt{\pi} \sigma^2} \frac{\partial H(\alpha, \nu)}{\partial \nu} \quad [5]$$

or the derivative of [4] with respect to magnetic field  $h$ :

$$\frac{\partial I(\alpha, \nu)}{\partial h} = \frac{1}{\sqrt{\pi} \sigma^2} \operatorname{Re} [ iz w(iz) ] \quad [6]$$

Expressions [5] and [6] are exact and can be evaluated by means of Gautschi's algorithm (6,7) to evaluate  $w(iz)$ . For purposes of fitting, the factor  $1/(\sigma^2\sqrt{\pi})$  in [6] is replaced by an arbitrary fitting parameter to match the experimental height. The results of the calculations obtained with the expression below will be compared with those produced from computations based on expression [6] which are taken as a reference.

#### THE APPROXIMATED LINE SHAPE

The approximated Voigt profile  $H_{\text{APPR}}(\alpha, \nu)$  is given by (3):

$$H_{\text{APPR}}(\alpha, \nu) = \frac{a}{\sqrt{\pi}} \frac{1}{(\nu^2 + a^2)} \frac{a}{2\sqrt{\pi}} \frac{3\nu^2 - a^2}{(\nu^2 + a^2)^3} \quad [7]$$

which is valid in the range  $a \gg 1/\sqrt{2}$ .

By substituting [7] in [5], the resulting approximate EPR line shape is:

$$\begin{aligned} \pi\sigma^2 \frac{\partial I(\alpha, \nu)}{\partial h} &= \frac{\sqrt{\pi}}{2} \frac{\partial H_{\text{APPR}}(\alpha, \nu)}{\partial \nu} \\ &= -a \frac{\nu}{(\nu^2 + a^2)^2} + 3a \frac{\nu(a^2 - \nu^2)}{(\nu^2 + a^2)^4} \end{aligned} \quad [8]$$

The approximate absorption line [8] for the EPR line shape is easier to evaluate than the exact expression [6] and, as will be seen, gives a good estimation for the Lorentzian and Gaussian widths.

FWHMs of the solution EPR line are obtained by fitting the approximated expression [8] to the digitalized data of the line. The results in units of 0.05 G (5) are:  $\Gamma_L = 3.299 \pm 0.282$ ,  $\Gamma_G = 0.606 \pm 0.032$ . These results must be compared with those obtained from expression [6] :  $\Gamma_L = 3.282 \pm 0.167$ ,  $\Gamma_G = 0.665 \pm 0.019$  which have been taken as reference.

The FWHMs in Gauss of the EPR line are presented in Table I; the values of  $\alpha$  obtained by means of expression [2] are 4.138 for the reference and 4.579 for the approximation. These values of  $\alpha$  are large enough to fulfill the condition  $\alpha \gg 1/\sqrt{2}$  for the application of the approximated expression [8] to deconvolute EPR lines whenever these are more Lorentzian than Gaussian. The results shown in Table I indicate that expression [8] can be safely used to estimate the width parameters of a mildly Gaussian-convoluted Lorentzian line quickly.

TABLE I

	Expression [8]	Expression [6]	$\frac{\Gamma_{[8]} - \Gamma_{[6]}}{\Gamma_{[6]}}$
$\Gamma_L$	$0.165 \pm 0.014 \text{ G}$	$0.164 \pm 0.008 \text{ G}$	0.61 %
$\Gamma_G$	$0.030 \pm 0.002 \text{ G}$	$0.033 \pm 0.001 \text{ G}$	-9.10 %

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#### REFERENCES

- 1.- W. GORDY, "Theory and Applications of Electron Spin Resonance" p. 104, John Wiley, 1980.
- 2.- W. VOIGT, *S. B. Bayer Acad. Wiss.* 603 (1912).
- 3.- H. FLORES-LLAMAS, A. CABRAL-PRIETO and H. JIMENEZ-DOMINGUEZ, *Nuclear Instruments and Methods*, to be published.
- 4.- C. A. JR. HUTCHISON, *J. Chem. Phys.* 57, 546 (1953).
- 5.- R. S. ALGER, "Electron Paramagnetic Resonance: Techniques and Applications" p. 304, Interscience Publishers, 1968.
- 6.- H. FLORES-LLAMAS, A. CABRAL-PRIETO, H. JIMENEZ-DOMINGUEZ and A. BRAVO-ORTEGA, *Nucl. Instr. and Meth.* A287, 557 (1990).



- 7.- W. GAUTSCHI, *SIAM J. Numer. Anal.* 7, 187 (1970).
- 8.- A. CABRAL-PRIETO, H. JIMENEZ-DOMINGUEZ, L. GONZALEZ-TOVANY, S. GALINDO, H. FLORES-LLAMAS AND M. TORRES-VALDERRAMA, *Journal of Magnetic Resonance*, to be published.
- 9.- D. W. POSENER, *Austr. J. Phys.* 12, 184 (1959).
- 10.- C. J. BATTY, S. D. HOATH and B. L. ROBERTS, *Nucl. Instr. and Meth.* 137, 179 (1976).
- 11.- S. GANAPATHY and V. PARTHASARATHI, *Indian J. of Pure and Appl. Phys.* 15, 63 (1977).
- 12.- J. T. DAVIES and J. M. VAUGHAM, *Astrophys. J.* 137, 1302 (1963).
- 13.- W. MEISEL, *Phys. Stat. Sol. (b)*, 43, k129 (1971).
- 14.- G. K. WERTHEIM, M. A. BUTLER, K. W. WEST and D. N. E. BUCHANAN, *Rev. Sci. Instrum.* 45, 1369 (1974).
- 15.- J. J. PEYRE and G. PRINCIPI, *Nucl. Instr. and Meth.* 101, 605 (1972).