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Fitting of the Derivative Voigt ESR Line under Conditions of Modulation Broadening

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An analysis is made of the effect of the magnetic-field-modulation amplitude on the Voigt lineshape in electron spin resonance spectroscopy. The problem is solved numerically using the Fourier expansion method. Only the coefficient of the first harmonic in the Fourier expansion, corresponding to the output of the phase-sensitive detector, is analyzed. The modulation-broadened first-derivative Voigt ESR line, here after referred to as the derivative Voigt, is fitted with the sum of a first-derivative Gaussian function and a first-derivative Lorentzian function of equal linewidths to extract the Lorentzian contribution of the line. Fitting to the sum is applicable as long as the amplitude of modulation is less than the true peak-to-peak linewidth of ESR line. Modulation broadening substantially contributes only to the derivative Gaussian component of the derivative Voigt line. The same effect is observed for the modulation-broadened derivative Lorentzian lineshape, which also can be fitted to the sum function. The linewidth of the Lorentzian component of the modulation-broadened derivative Lorentzian is constant if the modulation amplitude is less than the peak-to-peak linewidth. For the modulation-broadened derivative Voigt line, the goodness of the fit depends on the ratio of the Gaussian component to the Lorentzian component of the derivative Voigt line. When the Lorentzian component of the derivative Voigt is dominant, the linewidth of the Lorentzian component can be extracted for a broader range of the modulation amplitudes than when the Gaussian component is dominant.

INTRODUCTION

Magnetic-field modulation is used in most conventional continuous-wave electron spin resonance spectrometers (*1*). For very weak ESR signals, magnetic-field modulation substantially increases the signal-to-noise ratio by increasing ESR signal height, but, unfortunately, it distorts the shape of ESR line. Therefore, in order to get correct results from an ESR spectrum, it is very important to know the effect of modulation on ESR lineshape. The effect of modulation on the Lorentzian and Gaussian lineshape is well known. In the case of the Lorentzian lineshape, the modulation effect can be described by a closed analytical expression (*2*). But for a Gaussian lineshape, it is not possible to obtain a simple closed analytical expression and the problem must be expressed numerically (*3*). The ESR spectroscopy of spin labels generates a lineshape that is neither the Lorentzian nor the Gaussian, but a mixture of them (*4*). This mixture of the Gaussian and Lorentzian lineshapes is caused by both inhomogeneous and homogeneous broadening. A common representation of an inhomogeneously broadened ESR lineshape is a derivative of a convolution of the Lorentzian spin packet line with a Gaussian function and is referred to here as the derivative Voigt lineshape (*4–7*). In this paper we study the effect of modulation on the derivative Voigt lineshape using the Fourier expansion approach. Only the first coefficient in the Fourier expansion, which corresponds to the output of the phase-sensitive detector, is analyzed numerically on a computer.

Recently, it has been shown that by fitting the derivative Voigt lineshape with a sum function of the derivative of the Lorentzian and derivative of the Gaussian, it is possible to separate the Lorentzian linewidth and the Gaussian linewidth of the ESR line (*8*). In the present work we apply the same approach to the fitting of both the modulation-broadened derivative Lorentzian and the modulation-broadened derivative Voigt lineshape using the sum function. The limits of such an approach are discussed and a proper measuring procedure is suggested.

THEORY

The normalized unsaturated Voigt absorption lineshape is given by (*4*)

$$V[\nu(t)] = \frac{2\chi}{\sqrt{3\pi^3}\,\Delta B_{\mathrm{pp}}^{\mathrm{G}}} \times \int_{-\infty}^{\infty} \frac{e^{-x^2}}{1 + (2/3)\chi^2[\nu(t) - x]^2}\,dx, \quad [1]$$

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where

$$\nu(t) = \sqrt{2}\,\frac{[B_s(t) - B_0]}{\Delta B_{pp}^{G}}, \quad x(t) = \sqrt{2}\,\frac{(B' - B_0)}{\Delta B_{pp}^{G}}. \quad [2]$$

$B_s(t)$ represents the sweeping applied magnetic field, B_0 is the center of the line, and χ is the ratio of the Gaussian peak-to-peak linewidth component of the Voigt, ΔB_{pp}^{G}, to the Lorentzian peak-to-peak linewidth component of the Voigt, ΔB_{pp}^{L}:

$$\chi = \frac{\Delta B_{pp}^{G}}{\Delta B_{pp}^{L}}. \quad [3]$$

If we modulate the external magnetic field with $(1/2)B_m\cos(\omega t)$ and scan linearly and slowly through resonance with magnetic field $B_s(t)$, we get

$$\nu(t) = \sqrt{2}\,\frac{[B_s(t) + (1/2)B_m\cos(\omega t) - B_0]}{\Delta B_{pp}^{G}}. \quad [4]$$

Fourier analysis gives

$$V(t) = \sum_{n=0}^{\infty} a_n(\chi, B_m, B_\delta)\cos(n\omega t), \quad [5]$$

where $B_\delta = B_S - B_0$. The Fourier amplitudes are then given by

$$a_n = \frac{\omega}{\pi}\int_{-\pi/\omega}^{\pi/\omega} \cos(n\omega t)V(t)dt = \frac{1}{\pi}\int_{-\pi}^{\pi} \cos(n\theta)V(\theta)d\theta, \quad [6]$$

where $\theta = \omega t$.

The output of the phase-sensitive detector is proportional to the coefficient of the first harmonic:

$$a_1 = \frac{2\chi}{\sqrt{3\pi^5}\,\Delta B_{pp}^{G}}\int_{-\pi}^{\pi}\int_{-\infty}^{\infty} \frac{e^{-x^2}\cos\theta\, d\theta\, dx}{1 + (2/3)\chi^2[\nu(t) - x]^2} \quad [7]$$

The derivative Voigt lineshape [7], when B_m equals zero, can be well approximated by the variably weighted sum of the derivatives of the Gaussian and Lorentzian lineshapes (*4, 8*)

$$V^{S}[B_s(t)] = V_{pp}\left[\eta\frac{8\zeta}{(3 + \zeta^2)^2} + (1 - \eta)\frac{\sqrt{e}}{2}\,\zeta e^{-\zeta^2/2}\right], \quad [8]$$

where

$$\zeta = 2\,\frac{[B_s(t) - B_0]}{\Delta B_{pp}^{V}}. \quad [9]$$

V_{pp} is the peak-to-peak amplitude, η is a normalized, variable weight term, and ΔB_{pp}^{V} is the peak-to-peak linewidth of the derivative Voigt line.

EXPERIMENTAL

Most of the results presented are the results of simulations. These calculations were compared with ESR experiments with two samples. The first sample was unoriented *trans*-polyacetylene. The ESR line of unoriented *trans*-polyacetylene has a Lorentzian lineshape and its peak-to-peak linewidth is 0.255 G at 250 MHz (*9*). The second sample was an air-equilibrated water solution of the spin label, perdeuterated 3-carbamoyl-2,2,5,5-tetramethylpyrrolin-1-yloxy (pDCTPO). The lineshape of pDCTPO is a derivative Voigt profile. The ratio of the Lorentzian peak-to-peak linewidth to the Gaussian peak-to-peak linewidth χ of an ESR line of pDCTPO solution depends on both the concentration of spin label and the concentration of dissolved oxygen (*10*).

Spectra were measured on a low-frequency ESR spectrometer at 250 MHz (*11*). The radiofrequency power was 1 mW (RF magnetic field about 40 mG), the modulation frequency was 5.12 kHz, the time constant was 0.1 s, and the data-point acquisition time was 0.1 s, with 256 points per acquisition.

RESULTS AND DISCUSSION

Figure 1 shows the first-harmonic ESR signal as a function of the applied magnetic field for a small modulation amplitude, simulated using Eq. [7]. The result of a typical fit of the sum function to a noiseless simulated spectrum is shown in the same figure. From the fit it is very difficult to discern the difference between two lines. The peak-to-peak height of the signal increases with amplitude of modulation B_m, reaches a maximum, and then slowly decreases (Fig. 2).

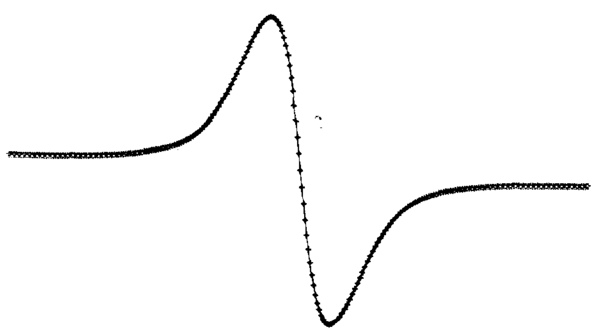

FIG. 1. Simulation of the modulated derivative Voigt lineshape. The modulation amplitude $B_m = 0.5\Delta B_{pp}^{V}(B_m = 0)$. The simulated line (—) and the fit to sum function (+) are given.

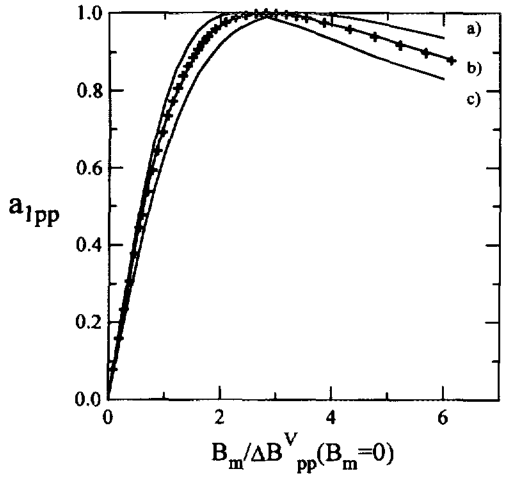

FIG. 2. Dependence of the peak-to-peak height normalized to the maximum peak-to-peak height a_{1pp} on the normalized modulation amplitude $B_m/\Delta B^V_{pp}(B_m = 0)$: (a) $\chi = 0.1$. (b) Experimental data from a 200 μM water solution of pDCTPO (+). Theoretical data $\chi = 0.85$ (—). (c) $\chi = 2$.

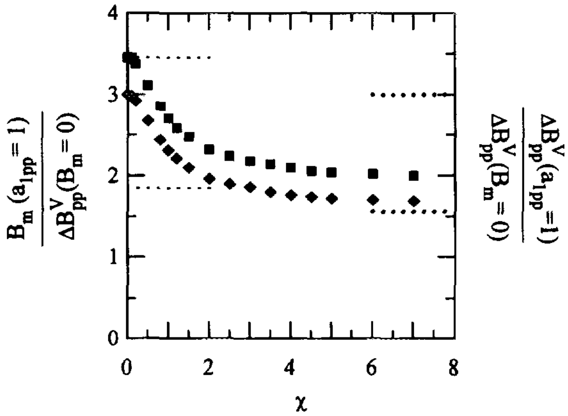

FIG. 3. (■) Modulation amplitude which gives the maximum peak-to-peak height normalized to the derivative Voigt peak-to-peak linewidth for $B_m = 0$: $B_m(a_{1pp} = 1)/\Delta B^V_{pp}(B_m = 0)$ plotted versus χ. The dashed lines represent the limits when $\chi = 0$ (the pure Lorentzian line) and $\chi = \infty$ (the pure Gaussian line). (♦) Modulation-broadened derivative Voigt peak-to-peak linewidth for the modulation amplitude which gives the maximum peak-to-peak height, $B_m(a_{1pp} = 1)$, normalized to the Voigt peak-to-peak linewidth when $B_m = 0$ plotted versus χ. The dotted lines represent the limits when $\chi = 0$ (the pure Lorentzian line) and $\chi = \infty$ (the pure Gaussian line).

Figure 2 shows the simulation of the amplitude-modulated Voigt line, peak-to-peak height normalized to the maximum peak-to-peak height, a_{1pp}, for three different values of χ. The experimental measurements of the normalized ESR signal height versus modulation amplitude B_m normalized to $\Delta B^V_{pp}(B_m = 0)$ for the 200 μM water solution of pDCTPO are also shown in Fig. 2. The fitted χ for the central line in the ESR spectrum of pDCTPO for very small B_m is 0.85 ($\Delta B^G_{pp} = 0.231$ G and $\Delta B^L_{pp} = 0.273$ G). The theoretical result for $\chi = 0.85$ is also shown in Fig. 2 as a solid line. As can be seen, the agreement is very good. Also, very good agreement holds between experimental and theoretical linewidth data (not shown). From Fig. 2 it can be seen that the amplitude of modulation which gives the maximum peak-to-peak height $B_m(a_{1pp} = 1)$ depends on χ. These values fall in the range limited by $1.848\Delta B^G_{pp}(B_m = 0)$ for the pure Gaussian and the $3.46\Delta B^L_{pp}(B_m = 0)$ for the pure Lorentzian, shown by the dashed lines in Fig. 3. $\Delta B^L_{pp}(B_m = 0)$ and $\Delta B^G_{pp}(B_m = 0)$ are the true peak-to-peak linewidths. At maximum height, the lines are considerably broadened (*2, 3*). Figure 3 also shows the simulation of modulation-broadened peak-to-peak linewidth at the amplitude of modulation value for the maximum height as a function of χ. Again, as expected, these values fall in the range limited by $1.56\Delta B^G_{pp}(B_m = 0)$ for the Gaussian and $3\Delta B^L_{pp}(B_m = 0)$ for the Lorentzian, shown by the dotted line in Fig. 3.

A second point of interest is the effect of the modulation broadening on the fitting of ESR lineshapes to the sum function V^s [8]. The effect of modulation broadening on a pure Lorentzian line is investigated. The solid lines in Fig. 4 show the results of the fitting of the modulation-broadened Lorentzian to the sum function. The modulation-broadened Lorentzian is calculated using the analytical expression for the first harmonic from Ref. (*3*). This is fitted to the sum function [8] according to the procedure for one ESR line suggested in Ref. (*8*). This means that only a region equal to $4\Delta B_{pp}$(obs) part of the lineshape around the line center

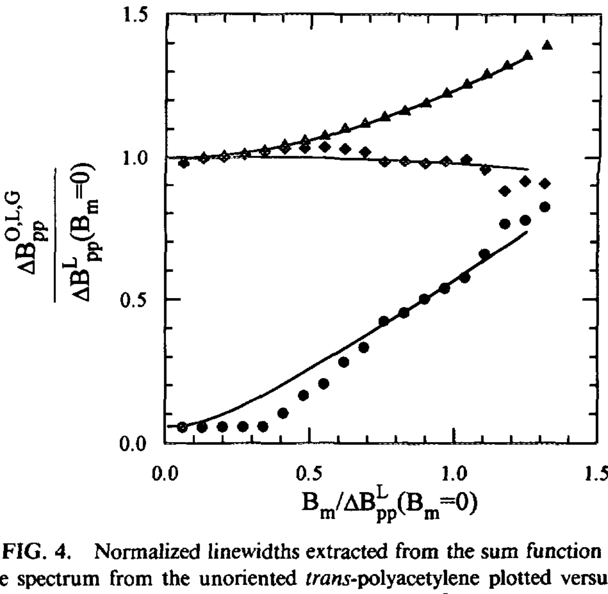

FIG. 4. Normalized linewidths extracted from the sum function fit to the spectrum from the unoriented *trans*-polyacetylene plotted versus the normalized modulation amplitude $B_m/\Delta B^L_{pp}(B_m = 0)$. ▲, $\Delta B^O_{pp}/\Delta B^L_{pp}(B_m = 0)$; ♦, $\Delta B^L_{pp}/\Delta B^L_{pp}(B_m = 0)$; ●, $\Delta B^G_{pp}/\Delta B^L_{pp}(B_m = 0)$. The lines represent the corresponding fitted parameters from the theoretically simulated modulation-broadened Lorentzian line.

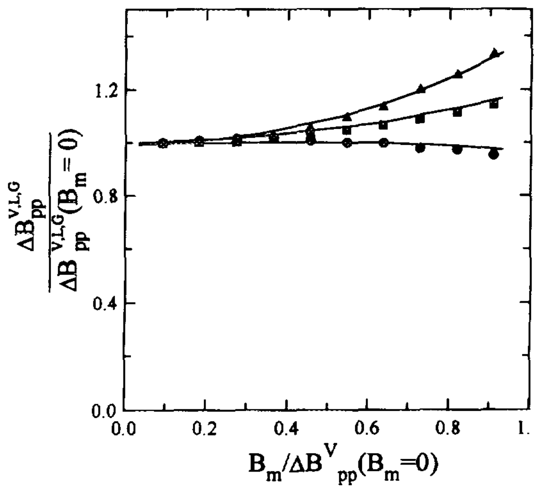

FIG. 5. Normalized linewidths extracted from the sum function fit to the spectrum from the 200 μM water solution of pDCTPO plotted versus the normalized modulation amplitude $B_m/\Delta B^V_{pp}(B_m = 0)$. ■, $\Delta B^V_{pp}/\Delta B^L_{pp}(B_m = 0)$; ●, $\Delta B^L_{pp}/\Delta B^L_{pp}(B_m = 0)$; ▲, $\Delta B^G_{pp}/\Delta B^L_{pp}(B_m = 0)$. The lines represent the corresponding fitted parameters from the theoretically simulated modulation-broadened Voigt line of $\chi = 0.85$.

is fitted. The value of χ is found from the fitted value of η using the expression (*8*)

$$\chi = \frac{-0.23627\eta^2 + 1.2838\eta - 1.08474}{\eta^2 - 1.33738\eta - 0.00201}. \quad [10]$$

Then, the Lorentzian and Gaussian linewidth can be found from the expressions (*4, 8, 12*)

$$\Delta B^L_{pp} = \Delta B^V_{pp} \frac{\sqrt{(1 + 4\chi^2)} - 1}{2\chi^2} \quad [11]$$

and $\Delta B^G_{pp} = \chi \Delta B^L_{pp}$. The observed peak-to-peak linewidth ΔB^O_{pp} is modulation broadened, but the fitted Lorentzian linewidth is constant to within 2% for $B_m/\Delta B^L_{pp}(B_m = 0) < 1$. To within the small change seen in Fig. 4, the Lorentzian linewidth assigned by this fitting procedure is unaffected by modulation broadening. The increase of the modulation amplitude contributes to the increase of the Gaussian component. Figure 4 also shows the experimental results for an unoriented *trans*-polyacetylene sample. The lineshape of its signal is Lorentzian. The agreement between the experimental and theoretical data is very good.

The results from the fitting of the modulation-broadened Voigt lineshape $\chi = 0.85$ are shown in Fig. 5. Again, it can be seen that ΔB^L_{pp} is far less affected than ΔB^V_{pp} and ΔB^G_{pp}. The same effect is observed in experimental studies of a nitroxide spin label in sodium dodecyl sulfate micelles (*13*). The deviation of the apparent Lorentzian width from the zero modulation ($B_m = 0$) Lorentzian linewidth increases with χ. Figure 5 also shows the experimental ESR data from a 200 μM water solution of pDCTPO. The agreement between theory and experiment in this case is very good.

In Fig. 6A we plot the deviation of the fitted value of the modulation-broadened line from the $B_m = 0$ Lorentzian linewidth as a function of χ for several different amplitudes of modulation normalized to the peak-to-peak observed Voigt linewidth when B_m equals zero. We define this deviation as $[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0]/\Delta B^L_{pp}(B_m = 0)$. The deviation is very small, less than 1%, when the amplitude of modulation is less than or equal to a half of the peak-to-peak observed Voigt linewidth when $B_m = 0$. If the amplitude of modulation is bigger than half of $\Delta B^V_{pp}(B_m = 0)$, the deviation increases both with χ and B_m. If we take a ratio of the difference between the Lorentzian linewidths $\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)$ to the observed Voigt linewidth ΔB^V_{pp}, we find that the ratio is nearly independent of χ. Figure 6B shows the ratio $[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)]/\Delta B^V_{pp}$ as a function of χ for several different amplitudes of modulation normalized to the peak-to-peak derivative Voigt linewidth at $B_m = 0$. The ratio $[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)]/\Delta B^V_{pp}$, which depends only on the amplitude of modulation, is shown in Fig. 7 as a function of the normalized amplitude of modulation $B_m/\Delta B^V_{pp}(B_m = 0)$. From both Fig. 6A and Fig. 7 it can be

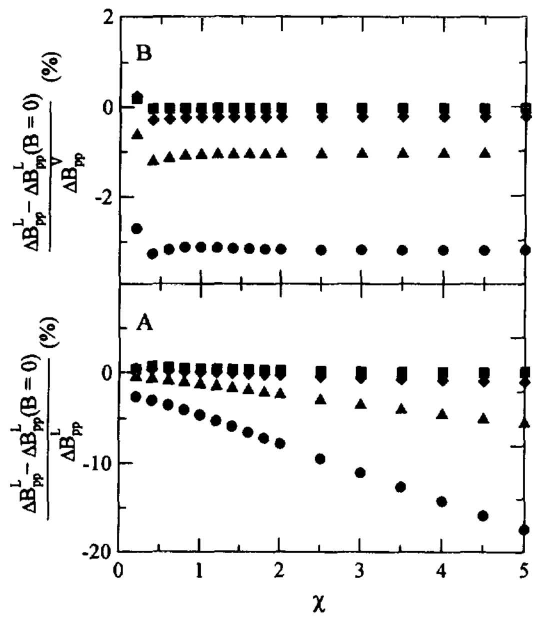

FIG. 6. (A) The deviation of the Lorentzian linewidth extracted from a fit of the sum function to a Voigt line from the unmodulated Lorentzian linewidth $[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)]/\Delta B^L_{pp}(B_m = 0)$ as a function of χ. ■, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.25$; ♦, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.5$; ▲, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.75$; ●, $B_m/\Delta B^V_{pp}(B_m = 0) = 1$. (B) The ratio of the difference between the Lorentzian linewidth extracted from a fit of the sum function to a Voigt line and the zero modulation Lorentzian linewidth to the simulated Voigt linewidth $\Delta B^V_{pp}[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)]/\Delta B^V_{pp}$ as a function of χ. ■, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.25$; ♦, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.5$; ▲, $B_m/\Delta B^V_{pp}(B_m = 0) = 0.75$; ●, $B_m/\Delta B^V_{pp}(B_m = 0) = 1$.

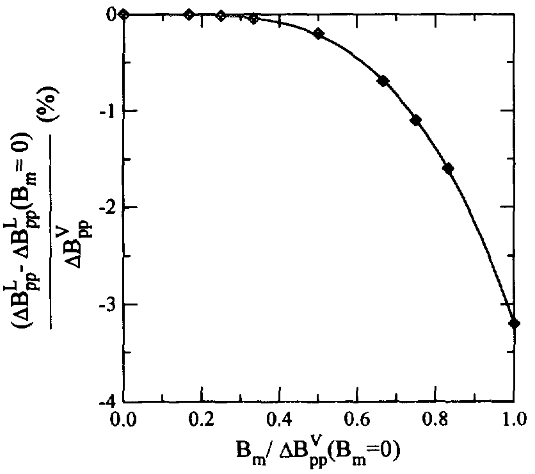

FIG. 7. The ratio of the difference between the Lorentzian linewidth extracted from a fit of the sum function to a Voigt line and the unmodulated Lorentzian linewidth to the simulated Voigt linewidth $\Delta B^V_{pp}[\Delta B^L_{pp} - \Delta B^L_{pp}(B_m = 0)]/\Delta B^V_{pp}$ as a function of the normalized modulation amplitude $B_m/\Delta B^V_{pp}(B_m = 0)$.

seen that the effect of modulation on the sum-function-derived Lorentzian linewidths is negligible when the amplitude of modulation is less than half of $\Delta B^V_{pp}(B_m = 0)$.

CONCLUSIONS

The effect of modulation on the Voigt lineshape depends on the ratio of the Gaussian linewidth to the Lorentzian linewidth, χ. The value of modulation amplitude at which the height of the signal reaches its maximum varies with χ. These values fall in the range of $1.848\Delta B^G_{pp}(B_m = 0)$ for the pure Gaussian and $3.46\Delta B^L_{pp}(B_m = 0)$ for the pure Lorentzian line. The peak-to-peak linewidth of a modulation-broadened derivative Voigt observed at the modulation amplitude that gives the maximum peak-to-peak height also depends on χ. The values of these linewidths fall in the range of $1.56\Delta B^G_{pp}(B_m = 0)$ for the pure Gaussian and $3\Delta B^G_{pp}(B_m = 0)$ for the pure Lorentzian line. From the measurement of amplitude of modulation at which peak-to-peak signal height reaches its maximum one can extract the value of χ. Then, the Lorentzian linewidth can be easily obtained from [11].

It is shown that the modulation-broadened Lorentzian and Voigt lineshapes can be fitted well to the sum function, if the modulation amplitude is less than the peak-to-peak linewidth measured when B_m goes to 0. It is found that in this region the modulation broadening contributes to the Gaussian linewidth. Finally, for a modulation amplitude less than half the peak-to-peak linewidth, the Lorentzian peak-to-peak linewidth can be found from the modulation-broadened Voigt line of any χ by fitting to the sum function. The deviation of the fitted Lorentzian linewidth is then less than 1%. The fitting procedure described allows the use of much higher amplitude of modulation than expected without the distortion of the Lorentzian linewidth.

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