

Communication

Lineshapes of spin exchange broadened EPR spectra

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Abstract

An unexplained residual in the fits of theoretical and experimental spectra of exchange broadened nitroxide spin probes reported by Robinson et al. [J. Magn. Reson. 138 (1999) 199] is shown to be understood by inclusion of theoretically predicted lineshape changes into the fitting routine. These lineshape changes provide an additional estimate of the spin exchange frequency that is independent of linewidth methods.

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Nonlinear spectral line fitting has become a powerful method in ESR data analysis [1–4]. Among the benefits of the approach are: (1) increased accuracy in the determination of EPR parameters even though they are accessible using conventional approaches, (2) increased sensitivity, (3) separation of inhomogeneous and homogeneous contributions to the spectral linewidth, and (4) access to EPR parameters otherwise not readily obtainable. Item (1) has two aspects. First, each spectrum is inherently analyzed more precisely and second, the ease of analysis permits better statistics by recording more spectra. Item (3) has been approached differently by different groups. Smirnov and Belford [2] have approximated the effects of inhomogeneous broadening due to unresolved hyperfine structure by assuming a Gaussian profile and fitting to a Voigt shape. Halpern et al. [1] have similarly assumed a Gaussian profile, but have used a Gaussian–Lorentzian sum function to approximate the Voigt. Robinson et al. [4] have improved the treatment by explicitly including the unresolved hyperfine structure. Under item (2), increased sensitivity may be attained by increasing the magnetic field modulation amplitude at the cost of distorting the line [5]; however, this distortion was shown to be due to an

added Gaussian component for modest modulation amplitudes and could be corrected by the same techniques used to correct for unresolved structure [6]. In a recent paper, Robinson et al. [4] have developed a more rigorous treatment of field modulation which allows for fitting severely over modulated spectra.

Despite the obvious advantages, the EPR community has remained resistant to adopting spectral fitting methods. It is therefore of particular interest that Robinson et al. [4] have packaged the entire fitting routine in a commercially available software program that could make the procedure more accessible to other labs.

The fitting procedure described in [4] is impressive indeed; however, there was a small residual in both simulated and experimental spectra that remained unexplained. The purpose of this Communication is to point out that this residual is predicted by theory and could be readily incorporated into the fitting routine. As the authors suggested [4], the residual is due to spin exchange and, in fact, yields an independent method to estimate the spin exchange frequency. Thus, incorporating the spin exchange effect into the spectral analysis would contribute to item (4) above.

The theory of spin exchange between free radicals in liquids has been well established [7–11]. Most aspects of the theory have been reasonably verified experimentally, except for the line shifts which show discrepancies

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currently under discussion [1,3,4,12]. For a detailed introduction to the subject see Molin et al. [11] and for a recent update see the Introduction of [3]. According to all theories the eigenvalues of the spin exchange spin Hamiltonian are complex, which implies that the lineshape of the spin exchange broadened EPR line is no longer purely Lorentzian. Under conditions common to spin exchange between nitroxide free radicals in solution, the spectrum is given by a complex sum over all of the lines of the spectrum. This equation is given, for example, by Eq. (2.77) of [11] derived phenomenologically or Eq. (2.23) of [8] using a correlation function method. Under conditions of slow exchange $\omega_{\text{ex}} \ll \gamma A_0$, where ω_{ex} is the spin exchange frequency, A_0 the hyperfine coupling constant in the absence of spin exchange, and γ the gyromagnetic ratio of the electron, Molin et al. [11] employing perturbation theory derived their Eq. (2.81) which details the departure of the lineshape from Lorentzian. We applied Molin's results to nitroxides in [3] to show that the lineshape was a sum of an absorption of Lorentzian shape and an spin-exchange induced "dispersion." The spin-exchange induced dispersion that depends upon hyperfine manifold is given by:

$$D_{M_I}^A(H) = \frac{4b_{M_I}[3 - \xi_{M_I}'^2]}{\pi[\Delta H_{\text{pp}}^L(\omega_{\text{ex}})_{M_I}]^2[3 + \xi_{M_I}'^2]}, \quad (1)$$

where

$$\xi_{M_I}' = 2 \frac{H - H(\omega_{\text{ex}})_{M_I}}{\Delta H_{\text{pp}}^L(\omega_{\text{ex}})_{M_I}}.$$

Here, M_I is the nitrogen nuclear spin quantum number; $H(\omega_{\text{ex}})_{M_I}$ is the resonance field of the M_I line under the influence of spin exchange; $\Delta H_{\text{pp}}^L(\omega_{\text{ex}})_{M_I}$ is the peak-to-peak linewidth of the M_I line; and the superscript A refers to the fact that the intensity (area) of the absorption part of the spectrum is normalized to unity. For ^{15}N nitroxide $b_{M_I} = \frac{2M_I\omega_{\text{ex}}}{\gamma A_0}$ and for ^{14}N , $b_{M_I} = \frac{M_I\omega_{\text{ex}}}{\gamma A_0}$. According to Eq. (1) the sign of the spin-exchange induced dispersion term varies from line to line in the spectrum as the sign of the nuclear spin quantum number. The dispersion¹ line is zero for a central line of a multiplet if such a line exists. We now turn to the residual observed by Robinson et al. [4]. The top spectrum in Fig. 1 is the result of simulating the spin exchange process using Currin's theory [3,8]. The spin exchange frequency $\omega_{\text{ex}} = 26.4$ MHz yielding $\omega_{\text{ex}}/\gamma = 1.5$ G was used in the simulation, while the nitrogen coupling constant A_0 is 22 G; thus the spectrum is still in the slow spin exchange limit. The result of the fitting this simulated spectrum to a pure Lorentzian absorption lineshape is also shown in the figure. The fit is not very good and the difference

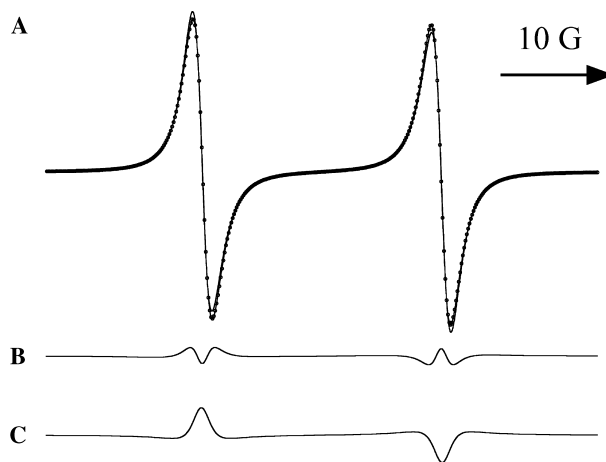


Fig. 1. (A) Simulated slow exchange spectrum with an exchange frequency of 26.4 MHz and a hyperfine splitting of 22 G (line) and the best of this simulated spectrum to a pure Lorentzian absorption lineshape (line with circles). (B) The residual, which is the difference between the simulated spectrum, and the fit. (C) The spin-exchange induced dispersion that brings the fitted curve into agreement with the simulated curve in Fig 1A.

between the spectrum and the fit is shown in Fig. 1B. Compare this residual with that in Fig. 3 of [4]; they are of similar shapes and magnitude. If the simulated spectrum is fitted to the sum of Lorentzian absorption and dispersion lines centered at the same resonance field, where the dispersion components have opposite signs, the fit is essentially perfect and the residual is a straight line (not shown). This dispersion lines are shown in Fig. 1C. It should be emphasized that no additional adjustable parameters are needed to provide Fig. 1C; fixing ω_{ex} predicts the magnitude using Eq. (1). Including the dispersion in the fit has the additional benefit that it contains information on the spin exchange frequency. Following the development in [3] applied to a ^{15}N nitroxide yields the following relationship:

$$\frac{V_{\text{disp}}}{V_{\text{pp}}} = \frac{4\sqrt{3}\omega_{\text{ex}}}{\gamma A_0}, \quad (2)$$

where V_{disp} is the magnitude of the maximum amplitude of the dispersion component and V_{pp} is the peak-to-peak height of the first-derivative absorption peak. Eq. (2) is identical to that found for ^{14}N nitroxides; however, for other multiplicities, the coefficients on the right-hand side can be different [12]. From Eq. (2), another estimate of ω_{ex} is available from the spectrum. As a practical matter, we note that despite some advantages gained by using ^{15}N rather than ^{14}N nitroxides, in the matter of studying the dispersion term, one loses some information because one has one less line. In particular, especially with samples that absorb energy at microwave frequencies, normal dispersion; i.e., the component detected in phase with the microwave magnetic field can distort the spectrum. The normal dispersion contribution is easily corrected because the central line is affected

¹ Unless otherwise indicated, we use the simple term "dispersion" to mean the spin exchange induced additional term in Eq. (2.81) of [11].

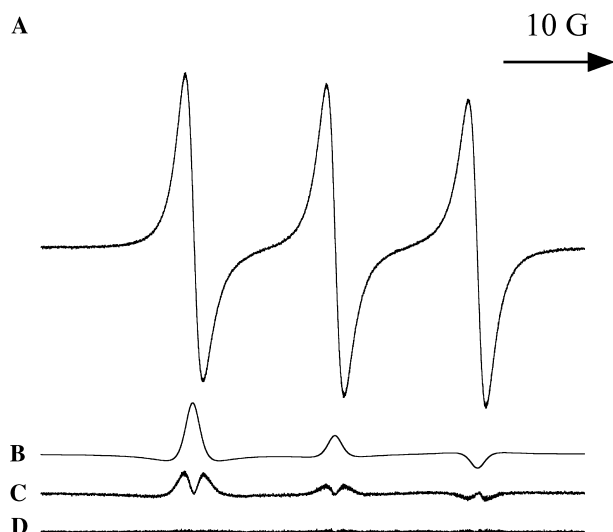


Fig. 2. (A) A spectrum of ^{14}N PADS under slow spin exchange. (B) The dispersion part of the fit consisting of both spin-exchange induced dispersion and normal dispersion. (C) The residual when the dispersion line, Eq. (1), is neglected. (D) The residual when the dispersion line, Eq. (1), is included.

only by the normal dispersion and not the spin exchange induced dispersion. This point is illustrated in Fig. 2A which shows an exchange-broadened spectrum of ^{14}N peroxyamine disulfonate. The spectrum was fit to a Lorentzian lineshape plus the dispersion component, Eq. (1), the latter of which is given in Fig. 2B; the residual is shown in Fig. 2D. The best fit, ignoring the dispersion term yields the residual in Fig. 2C again illustrating that the fit is rather poor. Fig. 2B shows the effect of instrumental dispersion, with a characteristic non-zero line for the central line. Such a spectrum may be corrected by subtracting $V_{\text{disp}}/V_{\text{pp}}$ for the central line from the other two. Carrying this out and applying Eq. (2) yields $\omega_{\text{ex}} = 32.38$ MHz and 31.78 MHz from the low- and high-field lines, respectively. This may be compared with $\omega_{\text{ex}} = 31.83$, 31.61 , and 31.65 MHz from the broadening of the low-, central-, and high-field lines, respectively. It might seem that incorporating the dispersion term into the fitting routine would only provide a solution to the lineshape problem for slow spin exchange since the perturbation treatment that revealed the term is only valid in that region. However, one of the most surprising results in our treatment of spectra that extended to much higher values of ω_{ex} was that only the same two terms, absorption plus dispersion, described the simulated, or experimental spectra all the way up to the point at which the lines merged into a single line [13]. The ratio in Eq.(2) departs from linearity, the outer lines in a ^{14}N spectrum broaden more rapidly than the central

line, and the doubly integrated intensity of the outer lines decrease while the central line grows, but only two components are needed to fit the lines. Thus, from the point of view of obtaining a fit, only the dispersion term (one for each line) would need to be added to the fitting routine.

Acknowledgments

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