

# Distant-dipole field in liquids and diffusion: A perturbative approach

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A perturbative approach is employed to solve the Bloch-Torrey equations in the presence of distant-dipole fields in nuclear magnetic resonance. The procedure, although only carried out to first order in the perturbation parameter  $a=1/k^2D\tau_d$ , could, in principle, be generalized to higher orders. Here  $D$  is the diffusivity,  $\tau_d$  the dipolar demagnetization time, and  $k$  is the wave vector of the spatial modulation of magnetization produced by the magnetic field gradient. The results are especially interesting for dilute binary mixtures consisting of molecular species with different diffusivities. In this case the calculated two-dimensional correlation spectroscopy revamped by asymmetric  $Z$ -gradient echo detection spectra are shown to be free from some inadequacies resulting from a simplistic application of standard approximations. © 2005 American Institute of Physics. [DOI: 10.1063/1.1832599]

## I. INTRODUCTION

The role of diffusion in the presence of distant-dipole<sup>1</sup> fields in liquids has been studied from various points of view focusing on different aspects of the problem. Since the equations appear to defy any possibility of a simple analytical solution, various approximations have been employed in the derivation of expressions describing the role of diffusion. An experimental test of some of these approximations<sup>2</sup> has recently unveiled inadequacies that become quite obvious when comparing with experimental two-dimensional (2D) spectra of binary mixtures obtained by the correlation spectroscopy revamped by asymmetric  $Z$ -gradient echo detection (CRAZED) (Ref. 3) pulse sequence.

In a pioneering paper Ardelean and Kimmich<sup>4</sup> proposed an expression for the signal evolution during the observation period of the CRAZED pulse sequence. In their treatment, diffusion during the observation period does not act directly on the transverse component of magnetization but only indirectly through the spatially modulated dipolar field, which is proposed to be attenuated in a special manner. Ramanathan and Bowtell<sup>5</sup> noticed that in a regime where  $a=1/k^2D\tau_d \ll 1$ , where  $k$  denotes the wave vector of the spatial modulation of magnetization caused by the magnetic field gradient,  $D$  denotes the diffusivity, and  $\tau_d$  denotes the dipolar demagnetization time, analytical solutions of the Bloch-Torrey equations are possible. They further demonstrated that the Ardelean-Kimmich expression could be obtained from the Bloch-Torrey equations only in the limit  $a \ll 1$ . However, no clue was offered as to what order of perturbation was involved, in what range of values of the observation time the solution could be expected to be valid, or how to generalize the procedure to higher orders.

In this paper we attempt to answer these questions in a systematic manner using a perturbative approach to the solution of the Bloch-Torrey equations in the presence of

distant-dipole fields. The results are especially interesting when applied to the calculation of 2D CRAZED spectra of dilute binary mixtures consisting of molecular species with different diffusivities. In this case, some of the inadequacies resulting from a simplistic application of standard approximations<sup>6</sup> are shown to be removable by the present approach.

## II. THEORY

Figure 1 shows schematically a CRAZED pulse sequence involving two  $\pi/2$  pulses. The first and second magnetic field gradient pulses have width  $\delta$  and, respectively, amplitudes  $G$  and  $pG$ , where  $p$  is an integer. Furthermore, the duration  $\delta$  of the gradient pulses is assumed, for simplicity, to be negligible compared with the evolution time  $t_1$  and the observation time  $t_2$ .

In a frame rotating at the Larmor frequency of a single species of spins, with magnetogyric constant  $\gamma$ , and assuming polarizing field and gradients applied along the  $z$  axis, one is interested in the time evolution of the transverse magnetization density  $M^+ = M^x + iM^y$ . After the application of the first  $(\pi/2)_x$  pulse and the short gradient pulse of area  $G\delta$ , the magnetization density becomes  $M^+(z, \delta) = iM_0 \exp(-i\gamma G\delta z)$  with  $M^z=0$ , where  $M_0$  denotes the uniform thermal equilibrium magnetization density. This magnetization helix is attenuated at later times by diffusion and relaxation.

In order to simplify the mathematical expressions and emphasize the role of diffusion, we choose to first ignore relaxation postponing for the moment the discussion of its effects. This is equivalent to assume that the relevant evolution and observation times are short compared with  $T_1$  and  $T_2$ , where  $T_2$  and  $T_1$  denote transverse and longitudinal relaxation times, respectively. Moreover, this condition is approximately satisfied for the systems we will be discussing.

Consider first the evolution of the transverse magnetization density  $\Gamma^+(z, t_2)$  assuming that distant-dipole effects are

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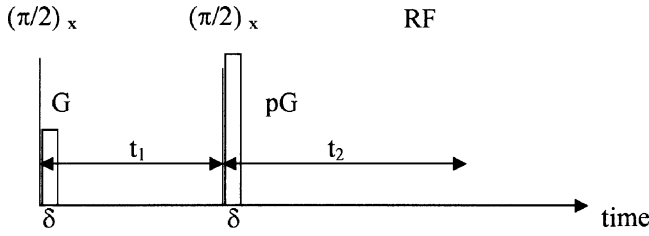


FIG. 1. Gradient and radio frequency pulses in the CRAZED sequence.

absent. After the evolution time  $t_1$  and the application of the second rf and gradient pulses, the solution of the Bloch-Torrey equation yields,<sup>2</sup> for  $t_2 > 0$ :

$$\Gamma^+(z, t_2) = \frac{i}{2} M_0 e^{-k^2 D t_1} [e^{-i(p+1)kz} e^{-(p+1)^2 k^2 D t_2} - e^{-i(p-1)kz} e^{-(p-1)^2 k^2 D t_2}] \quad (1)$$

where  $k = \gamma G \delta$  and  $D$  denotes diffusivity. The presence of the distant-dipole field for  $t_2 > 0$ , determined by  $M^z(z, t_2)$ , requires the solution of a modified Bloch-Torrey equation of the form

$$\frac{\partial M^+}{\partial t} = \frac{\partial^2 M^+}{\partial \zeta^2} + i a e^{-k^2 D t_1} e^{-t} \cos \zeta M^+, \quad (2)$$

where  $a = 1/k^2 D \tau_d$  is our perturbation parameter,  $\tau_d = 1/\gamma \mu_0 M_0$  denotes the dipolar demagnetization time, and  $\mu_0$  is the vacuum permeability. The solution of Eq. (2), which has been transformed to a dimensionless form by defining  $t = k^2 D t_2$  and  $\zeta = kz$ , should satisfy the initial condition  $M^+(\zeta, 0) = \Gamma^+(\zeta, t_2 = 0)$ .

We write the solution of Eq. (2) as the product  $M^+(\zeta, t) = \Gamma^+(\zeta, t) m^+(\zeta, t)$ , where the first factor, given by Eq. (1), is the solution in the absence of distant-dipole fields, and the second factor, which must satisfy the initial condition  $m^+(\zeta, 0) = 1$ , is to be determined in a perturbative fashion. Given that  $\Gamma^+(\zeta, t)$  satisfies a simple diffusion equation one has from Eq. (2)

$$\Gamma^+ \frac{\partial m^+}{\partial t} = \Gamma^+ \frac{\partial^2 m^+}{\partial \zeta^2} + 2 \frac{\partial \Gamma^+}{\partial \zeta} \frac{\partial m^+}{\partial \zeta} + i a e^{-k^2 D t_1} e^{-t} \cos \zeta \Gamma^+ m^+. \quad (3)$$

Considering specifically the important case  $p=2$ , the term containing  $e^{-(p+1)^2 t}$  in Eq. (1) can be neglected compared with  $e^{-(p-1)^2 t}$  for  $t \geq 1/4$ . Equation (2) can then be further simplified yielding

$$\frac{\partial m^+}{\partial t} \approx \frac{\partial^2 m^+}{\partial \zeta^2} + 2i \frac{\partial m^+}{\partial \zeta} + i a e^{-t} \cos \zeta m^+, \quad (4)$$

where we have defined  $\alpha = a e^{-k^2 D t_1}$ .

We can attempt an iterative procedure to obtain a solution of Eq. (4) valid to first order in  $a$ . To that end we adopt, as an approximant of order zero  $m_0^+(\zeta, t)$ , the solution of Eq. (4) corresponding to a simple precession in the dipolar field.

Thus, ignoring the spatial derivatives in Eq. (4) in this initial step of iteration we obtain

$$m_0^+(\zeta, t) = e^{i\alpha \cos \zeta \lambda_1(t)} \approx 1 + i\alpha \cos \zeta \lambda_1(t), \quad (5)$$

with  $\lambda_1(t) = \int_0^t e^{-\tau} d\tau$ . The spatial derivatives are taken into account in the second iteration step by substituting  $m_0^+(\zeta, t)$  from Eq. (5) into the right-hand side of Eq. (4). This gives

$$\frac{\partial m_1^+}{\partial t} = \frac{\partial^2 m_0^+}{\partial \zeta^2} - 2i \frac{\partial m_0^+}{\partial \zeta} + i a e^{-t} \cos \zeta m_0^+, \quad (6)$$

which can be solved to first order in  $a$  yielding

$$m_1^+(\zeta, t) = 1 + i\alpha [\lambda_1(t) - \lambda_2(t)] \cos \zeta - 2\alpha \lambda_2(t) \sin \zeta, \quad (7)$$

with  $\lambda_2(t) = \int_0^t \lambda_1(\tau) d\tau$ .

Application of this iteration procedure, keeping only terms linear in  $a$ , yields the following results for the first few successive approximants:

$$m_2^+ = 1 + i\alpha \cos \zeta (\lambda_1 - \lambda_2 + 5\lambda_3) - 2\alpha \sin \zeta (\lambda_2 - 2\lambda_3), \quad (8a)$$

$$m_3^+ = 1 + i\alpha \cos \zeta (\lambda_1 - \lambda_2 + 5\lambda_3 - 13\lambda_4) - 2\alpha \sin \zeta (\lambda_2 - 2\lambda_3 + 7\lambda_4), \quad (8b)$$

$$m_4^+ = 1 + i\alpha \cos \zeta (\lambda_1 - \lambda_2 + 5\lambda_3 - 13\lambda_4 + 41\lambda_5) - 2\alpha \sin \zeta (\lambda_2 - 2\lambda_3 + 7\lambda_4 - 20\lambda_5), \quad (8c)$$

where

$$\lambda_n(t) = \int_0^t \lambda_{n-1}(\tau) d\tau. \quad (9)$$

Higher order approximants can be readily obtained in the same fashion. Their general form is, to first order in  $a$ ,

$$m_n^+(\zeta, t) = 1 + i\alpha \cos \zeta \Lambda_n(t) - 2\alpha \sin \zeta \Gamma_n(t), \quad (10)$$

where  $\Lambda_n(t)$ ,  $\Gamma_n(t)$  are partial sums of, respectively, the temporal series  $\Lambda(t)$  and  $\Gamma(t)$ .

In order to calculate the observable signal amplitude only those terms of  $M^+(\zeta, t) = \Gamma^+(\zeta, t) m^+(\zeta, t)$  which, for  $\zeta \leq kL_z$ , survive an integration over  $\zeta$  need to be considered. Here  $L_z$  is the length of the sample along the  $z$  direction and we are assuming  $kL_z \gg 1$ . Denoting by  $\overline{M_n^+}(t)$  the integrated (normalized) signal corresponding to the approximant of order  $n$  we obtain

$$\begin{aligned} \overline{M_n^+}(t) &= -\frac{i}{2} e^{-k^2 D t_1} e^{-t} \overline{e^{-i\zeta} m_n^+(\zeta, t)} \\ &= \frac{\alpha}{4} e^{-t} [\Lambda_n(t) + 2\Gamma_n(t)], \end{aligned} \quad (11)$$

where the sum of the two temporal series of Eq. (10) can be inferred from Eq. (8) to be

$$\begin{aligned} \Lambda_n(t) + 2\Gamma_n(t) &= \lambda_1(t) + \lambda_2(t) + \dots + \lambda_{n+1}(t) \\ &= \sum_{j=1}^{n+1} \lambda_j(t). \end{aligned} \quad (12)$$

This result permits a simple analytical expression. From the definition of  $\lambda_j(t)$  in Eq. (9), the following recursion formula is obtained:

$$\lambda_{j+1}(t) = \frac{t^j}{j!} - \lambda_j(t), \quad \lambda_1(t) = 1 - e^{-t}. \quad (13)$$

Hence, the sum of the series can be seen to be simply the hyperbolic sine

$$\sum_{j=1}^{\infty} \lambda_j(t) = \sinh(t). \quad (14)$$

Substituting this result into Eq. (11) we obtain for the signal amplitude normalized by  $M_0$

$$\overline{M^+}(t_1, t_2) = \frac{e^{-k^2 D t_1}}{8k^2 D \tau_d} [e^{-k^2 D t_1} (1 - e^{-2k^2 D t_2})]. \quad (15)$$

For  $k^2 D \tau_d \gg 1$ , the above expression coincides with the formula derived by Ardelean and Kimmich<sup>4</sup> when a small argument expansion of the Bessel functions is employed.

From our approach we conclude that  $\overline{M^+}(t_1, t_2)$  given by Eq. (15) is only a first order in  $a$  solution. Moreover it is only valid for a limited range of values of  $t_2$ . From Eq. (10) we notice that for the first order perturbation to be valid for all values of  $\zeta$  the conditions  $2\alpha\Gamma(t) \ll 1$  and  $\alpha\Lambda(t) \ll 1$  should be satisfied. This leads to the condition  $\sinh(t) \ll 2/\alpha$ , which for  $\alpha \ll 1$  can result in a sizable range of time. Moreover, the condition  $t \geq 1/4$  which permits to neglect, for  $p=2$ , the term  $e^{-(p+1)^2 t}$  in Eq. (1) is not too restrictive. It would cause Eq. (15) to somewhat miss a relatively small portion of the initial growth, which reaches its saturation value at  $t \approx 2.5$ . If one assumes, for example, a value  $\alpha=0.01$ , typical for the 2D experiments of Ref. 1, one could expect Eq. (15) to be valid in the range  $0.25 \leq t \leq 5.5$ , whereas for  $t > 5.5$  some departures are expected to become apparent requiring higher order terms in the perturbation series.

The derivation of Eq. (15) by the present perturbative method, rather than as a limit of the Ardelean and Kimmich<sup>4</sup> formula, permits considerable physical insight. In the latter case it is postulated that diffusion has no direct effect upon the transverse component of magnetization during observation time  $t_2$ . The effect is only indirect through the spatial modulation of dipolar field, which is proposed to be attenuated in a special manner. In the present approach no such postulate is employed. Moreover, it is shown that such assumption is not warranted in general. The decay of the transverse component of magnetization during  $t_2$ , caused by the term  $e^{-(p-1)^2 k^2 D t_2}$  in Eq. (1), is shown to be refocused by the term  $\sinh(k^2 D t_2)$ , resulting from the sum of the series of the Eq. (14), only if  $t_2$  is not too long. Thus, in the derivation of Eq. (15) from the Ardelean and Kimmich<sup>4</sup> formula the only condition required is  $a \ll 1$ , regardless of the value of  $t_2$ . In the present approach we show, however, that Eq. (15) cannot be valid for long values of  $t_2$  and we also estimate the range of its validity.

The perturbation approach can be extended, in principle, to a higher order in  $a$  but the summation of the temporal series appears to be quite difficult. It is possible, however, by

inspection of the terms which survive the spatial integration over  $\zeta$ , to conclude that the correction in  $a^2$  vanishes and that the next nonzero correction is of order  $a^3$ .

In order to explain some observed discrepancies in the interpretation of 2D CRAZED spectra,<sup>2</sup> we next consider a binary mixture of two molecular species with different diffusivities. Let  $A$  and  $B$  denote two molecular species with diffusivities  $D_{A(B)}$  and let  $2\omega$  denote the chemical shift between the two resonances, each consisting of a single line. The concentration of spins of each species is chosen, for simplicity, to be the same, permitting to set  $M_{0A} = M_{0B} = M_0$ . Furthermore, the carrier frequency of the nonselective  $\pi/2$  pulses is chosen to be equidistant from the two resonances.

In a reference frame rotating with the applied radio frequency one can write for the transverse magnetization, in the absence of distant-dipole fields, the following generalization<sup>2</sup> of Eq. (1):

$$\begin{aligned} \Gamma_{A(B)}^+(z, t_2) &= \frac{iM_0}{2} \\ &\times [e^{-i(p+1)kz} e^{\mp i\omega(t_1+t_2)} e^{-k^2 D_{A(B)} [t_1 + (p+1)^2 t_2]} \\ &- e^{-i(p-1)kz} e^{\pm i\omega(t_1+t_2)} e^{-k^2 D_{A(B)} [t_1 + (p-1)^2 t_2]}], \end{aligned} \quad (16)$$

where the upper sign corresponds to species  $A$  and the lower sign to species  $B$ .

A generalization of the modified Bloch-Torrey equations, for the case of two different diffusing species, yields

$$\begin{aligned} \frac{\partial M_A^+}{\partial t} &= \frac{\partial^2 M_A^+}{\partial \zeta^2} + i\Omega M_A^+ + ia \left[ e^{-k^2 D_A t_1} e^{-t} \cos \zeta \right. \\ &\left. + \frac{2}{3} e^{-k^2 D_B t_1} e^{-\rho t} \cos(\zeta - 2\omega t_1) \right] M_A^+, \end{aligned} \quad (17a)$$

$$\begin{aligned} \frac{\partial M_B^+}{\partial t} &= \rho \frac{\partial^2 M_B^+}{\partial \zeta^2} - i\Omega M_B^+ + ia \left[ \frac{2}{3} e^{-k^2 D_A t_1} e^{-t} \cos \zeta \right. \\ &\left. + e^{-k^2 D_B t_1} e^{-\rho t} \cos(\zeta - 2\omega t_1) \right] M_B^+, \end{aligned} \quad (17b)$$

where the following dimensionless quantities have been introduced:  $t = k^2 D_A t_2$ ,  $\rho = D_B/D_A$ ,  $a = 1/k^2 D_A \tau_d$ ,  $\Omega = \omega/k^2 D_A$ , and  $\zeta = kz$ . Equation (17) include the contribution of species  $B$  to the dipolar field sensed by spins of species  $A$  and the factor  $2/3$  results from the secular approximation<sup>2</sup> valid for  $2\omega \gg \gamma\mu_0 M_0$ .

Provided  $a \ll 1$  and  $a/\rho \ll 1$ , a perturbative approach is possible. Using the same steps leading to Eq. (15) the following expression, valid to first order in  $a$ , can be obtained:

$$\begin{aligned}
 \overline{M_{A(B)}^+}(t_1, t_2) &= \frac{e^{-k^2 D_{A(B)} t_1}}{8k^2 D_{A(B)} \tau_d} \\
 &\times \left[ e^{\pm i\omega(2t_1+t_2)} e^{-k^2 D_{A(B)} t_1} (1 - e^{-2k^2 D_{A(B)} t_2}) \right. \\
 &+ \frac{2}{3} e^{\pm i\omega t_2} e^{-k^2 D_{(A)B} t_1} \frac{2D_{A(B)}}{D_A + D_B} \\
 &\left. \times (1 - e^{-k^2 (D_A + D_B) t_2}) \right]. \quad (18)
 \end{aligned}$$

Transverse relaxation can be taken into account<sup>7</sup> by first multiplying Eq. (18) by  $e^{-(t_1+t_2)/T_{2A(B)}}$  and next substituting  $e^{-k^2 D_{A(B)} t_1}$  by  $e^{-(k^2 D_{A(B)} + 1/T_{2A(B)}) t_1}$  and  $e^{-k^2 D_{(A)B} t_1}$  by  $e^{-(k^2 D_{(A)B} + 1/T_{2(A)B}) t_1}$  inside the square brackets. Furthermore, the leading effect of  $T_1$  can be calculated using a dipolar field modified by  $T_1$  in our perturbative procedure. Defining  $\mu_{A(B)} = 1/k^2 D_{A(B)} T_{1A(B)}$ , the effect can be taken into account by replacing, within the square brackets of Eq. (18), the first term  $(1 - e^{-2k^2 D_{A(B)} t_2})$  by  $[2/(2 + \mu_{A(B)})][1 - e^{-(2 + \mu_{A(B)}) k^2 D_{A(B)} t_2}]$  and  $2D_A/(D_A + D_B)(1 - e^{-(D_A + D_B) k^2 t_2})$  by  $\{2D_A/[D_A + (1 + \mu_B)]D_B\}(1 - e^{-[D_A + (1 + \mu_B)D_B] k^2 t_2})$  in the second term of  $\overline{M_A^+}$ . Similarly, for the second term of  $\overline{M_B^+}$ , the roles of  $A$  and  $B$  are reversed.

Finally, the effect of relaxation in Eq. (15), valid for a single species, can be included by handling the terms inside and outside the square brackets in the same way as in Eq. (18).

### III. DISCUSSION

For  $a \ll 1$ , Eq. (15) can be obtained from the expression derived by Ardelean and Kimmich<sup>4</sup> by the following ansatz: (a) only the zeroth order approximant  $m_0^+$  is retained but the phase of the precession in the dipolar field is attenuated, in the presence of diffusion, by a factor  $(1 - e^{-2t})/2t$  leading to  $m_{AK}^+(\zeta, t) = e^{i\alpha \cos \zeta/2(1 - e^{-2t})}$  instead of  $m_0^+(\zeta, t) = e^{i\alpha \cos \zeta(1 - e^{-t})}$  and (b) diffusion is assumed to be absent from  $\Gamma_{AK}^+(\zeta, t)$  for  $t_2 > 0$ . One could be led to believe that applying the same ansatz to the  $A$  and  $B$  components of the dipolar field in a binary mixture [Assumption I ( $\alpha=0$ ) of Ref. 1], could similarly lead to Eq. (18). However, for  $D_A \neq D_B$ , this can be shown not to be true as illustrated by Fig. 2. Here we show calculated 2D CRAZED <sup>1</sup>H absolute values spectra obtained from a Fourier transform of  $\overline{M_A^+} + \overline{M_B^+}$ . The parameters are applicable to a dilute solution 0.04 M of 18 crown 6 in water-D<sub>2</sub>O [0.86% (V/V) of H<sub>2</sub>O and 99.14% (V/V) of D<sub>2</sub>O].<sup>2</sup> Since the perturbative parameters, for  $G = 8$  gauss/cm and  $\delta = 5$  ms, have values  $a_A = 9.4 \times 10^{-3}$  for 18 crown 6 and  $a_B = 2.7 \times 10^{-3}$  for water, it could be expected that a first order perturbation theory might have some validity for an appreciable range of the  $(t_1, t_2)$  plane. Unlike Assumption I ( $\alpha=0$ ) and other standard assumptions,<sup>6</sup> the amplitude ratios obtained from Eq. (18), without using any adjustable parameter, are quite realistic. For example, the  $AB/BA$  amplitude ratio, neglecting relaxation, is 1 for Eq. (18) and has a value of only 0.32 for Assumption I ( $\alpha=0$ ).

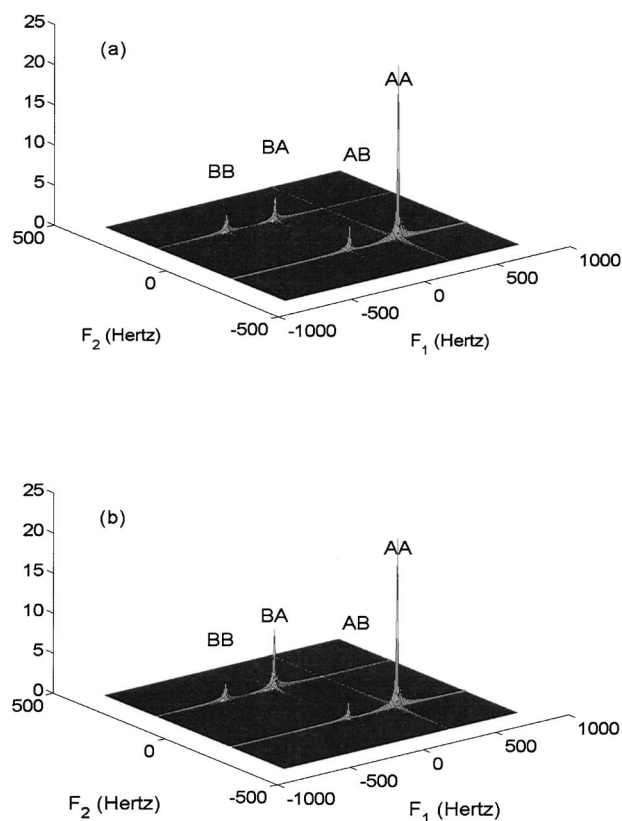


FIG. 2. Calculated absolute value <sup>1</sup>H 2D CRAZED spectra for a dilute 18 crown 6-H<sub>2</sub>O/D<sub>2</sub>O binary mixture. (a) Calculated from Eq. (18) including relaxation effects. (b) Calculated from Assumption I ( $\alpha=0$ ) including relaxation effects.

The inclusion of spin-spin relaxation has the effect of somewhat spoiling the agreement with the spectral data compared to the prediction of Eq. (18), where relaxation is neglected. This is not surprising since the amplitude ratios include contributions from regions of the  $(t_1, t_2)$  plane where the first order perturbation theory breaks down. The damping expected from the inclusion of higher order terms in  $a$  should tend to make the contribution from  $T_2$  comparatively less important. Nevertheless, the calculated ratios  $AA/AB = 5.1$ ,  $AA/BB = 11.5$ ,  $AB/BA = 1.3$ , and  $AB/BB = 2.3$  obtained from the first order theory, including relaxation and without any adjustable parameter, are still rewardingly close to the experimental values.<sup>2</sup>  $AA/AB = 6.7$ ,  $AA/BB = 11.5$ ,  $AB/BA = 0.84$ , and  $AB/BB = 1.7$ .

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