

Nuclear and Electron Relaxation in Magnetic Exchange Coupled Dimers: Implications for NMR Spectroscopy

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The transition probabilities and the lifetimes have been calculated for the levels arising from magnetic exchange coupling in the following electron spin pairs: $S_A = \frac{1}{2}$ - $S_B = \frac{1}{2}$; $S_A = \frac{1}{2}$ - $S_B = 1$; $S_A = \frac{1}{2}$ - $S_B = \frac{3}{2}$; $S_A = 1$ - $S_B = 1$. Such transition probabilities and lifetimes have been expressed as a function of the relaxation properties of the uncoupled spins in the assumption that magnetic coupling does not provide further relaxation pathways, and that the coupling frequency is large with respect to the electron relaxation rates of both spins. From the above values, nuclear relaxation as a function of the intensity of the external magnetic field has been calculated for nuclei dipole-coupled with either electron spin. The calculated nuclear relaxation dispersion has been then analyzed in terms of an “effective” electron relaxation time, the knowledge of which is important for NMR of magnetic coupled systems. The calculations provide a basis for understanding electron relaxation in magnetic-coupled dimers. Comparison with available experimental literature data is presented. © 1998 Academic Press

INTRODUCTION

Electronic relaxation in general, and at room temperature in particular, is a subtle matter which is understood only in principle. Monometallic systems in solution have been studied either through EPR (1–3) or, more often, through ¹H NMR in an extended range of magnetic fields (4). In the former case the transition linewidth and a rough estimate of the lifetime of the spin levels can be obtained. In the latter, an electron correlation time is obtained. The latter, in the case of $S > 1$, is a kind of average of different time constants of a multiexponential process, but is still meaningful for NMR spectroscopists since the value allows the discussion of nuclear relaxation as related to the particular metal ion (5). When the electron relaxation times are short, solid state mechanisms like either Raman (6) or Orbach (7) are considered to be operative (5). In contrast, when such times are

long, it is considered that modulation of the spin energy arises from solvent bombardment or molecular rotation (8–13). In the former case electron relaxation is not magnetic field dependent for the accessible fields, whereas it is in the latter. The different behavior essentially depends on the availability of low lying excited states (4). Along these lines, NMR spectroscopists can predict and understand nuclear relaxation.

Electron relaxation in dimetallic systems experiencing magnetic exchange coupling has been far less studied. By referring to the electron correlation time, or to an average value when $S > 1$, two limiting cases can be examined. The case of weak magnetic exchange coupling in heterodimetallic systems (i.e., the coupling energy is much smaller than the electron relaxation rate of the fast relaxing metal ion) has been treated as resulting in an additional electronic relaxation mechanism for the slow relaxing metal ion caused by the coupling to the fast relaxing metal ion, and accounted for by using perturbation theory (14–16). The fast relaxing metal ion was considered to be unaffected by the coupling (4, 17, 18). When magnetic exchange coupling is strong (i.e., the coupling energy is much larger than the electron relaxation rate of the fast relaxing metal ion) it had always been intuitively assumed that the electron relaxation rates of the two metal ions are the same and equal to the fast relaxing metal ion. We are now going to calculate the level lifetimes and total transition linewidths in some strongly coupled systems in terms of the relaxation times in the isolated ions. Then we calculate the nuclear relaxation of a nucleus sensing either metal ion at various magnetic fields and, from this, longitudinal (τ_1) and transverse (τ_2) effective electron correlation times for nuclear relaxation. The latter are the parameters of interest here.

The approach is that of evaluating the transition probabilities between pairs of $M_{S'}$ levels of the S' manifolds which originate from magnetic coupling, and their adiabatic linewidths (19). The overall electron relaxation turns out to display a multiexponential behavior which is analogous to

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that already encountered in $S > 1$ single-spin systems (9). Finally, the appropriate nuclear relaxation rate equations are calculated as a function of the external magnetic field, by using the simple Kubo and Tomita formalism for an electron–nuclear dipolar coupling (14, 17, 20). The calculated nuclear relaxation profiles can be fitted by assuming that the profiles are originated by a single electronic transition with effective electron correlation times τ_1 and τ_2 .

This research is of importance to magnetic resonance researchers in that (i) it provides a theoretical explanation of electron relaxation in the presence of magnetic exchange coupling, and (ii) it explains in a semiquantitative way why high resolution NMR can be performed on radicals and copper(II) compounds in the presence of magnetic coupling with fast relaxing metal ions like nickel(II) and cobalt(II).

THEORETICAL PART

The calculations have been performed under the conditions that:

(1) The dimeric system can be described by the Hamiltonian

$$\mathbf{H} = g_A \mu_e \mathbf{S}_A \cdot \mathbf{B}_0 + g_B \mu_e \mathbf{S}_B \cdot \mathbf{B}_0 + J \mathbf{S}_A \cdot \mathbf{S}_B, \quad [1]$$

where the first two terms are the Zeeman terms for the two ions and the last describes an isotropic exchange coupling interaction between the spin of metal A and that of metal B, S_A and S_B respectively. J is the isotropic coupling constant.

(2) The coupling frequency between spins is large in absolute value compared to the electronic relaxation rates but small compared to the modulation of the electron lattice interaction

$$|J|/\hbar \gg \tau_{sA}^{-1}, \tau_{sB}^{-1} \quad [2]$$

$$|J|/\hbar \ll \tau_{vA}^{-1}, \tau_{vB}^{-1}, \quad [3]$$

where $\tau_{sA}^{-1} = R_A$ and $\tau_{sB}^{-1} = R_B$ are the electron relaxation rates of uncoupled spins S_A and S_B respectively, and τ_{vA} , τ_{vB} are the corresponding correlation times for electron relaxation. The last condition practically means extreme narrowing limit for electron relaxation. This is often the condition encountered for fast relaxing metal ions, which are those of interest to NMR spectroscopists.

(3) It is further assumed that each electron spin relaxes with its own mechanisms independently of the occurrence of spin coupling. This is a key assumption, but it is reasonable within the frame of magnetic exchange coupling being a perturbation of the overall electronic structure of the uncoupled spin system. Finally, we assumed that the stochastic external fields causing relaxation of the individual ions do not appreciably correlate between themselves.

(4) The exchange coupling energy is much larger than the difference in the Zeeman energies. There is no theoretical requirement for this condition. However, as $|J| \gg$ Zeeman in most cases of interest, we limit ourselves to this case, also because the $|J| \ll$ Zeeman situation would yield results very similar to the uncoupled system.

J can be either positive or negative, and its absolute value can be smaller or larger than thermal energy, kT , but should be specified.

Calculation of Lifetimes and Transition Probabilities

We have considered in the present work the simplest case when the interactions of stochastic external fields with individual spins are isotropic. Thus, the time-dependent Hamiltonian for the interaction between the fluctuating fields and coupled spins can be written as (19)

$$\begin{aligned} \mathbf{H}(t) = & -1/2\gamma_e[S_{A+}H_{A+}(t) + S_{A-}H_{A-}(t) \\ & + 2S_{Az}H_{Az}(t) + S_{B+}H_{B+}(t) \\ & + S_{B-}H_{B-}(t) + 2S_{Bz}H_{Bz}(t)], \quad [4] \end{aligned}$$

where designations +, −, and z are used to distinguish the spherical components of spin operators \mathbf{S}_A and \mathbf{S}_B and random field operators $\mathbf{H}_A(t)$ and $\mathbf{H}_B(t)$. Our assumption about isotropic interaction also includes the conditions

$$\begin{aligned} (H_{Az}^2)_{av} = 1/2(H_{A+}^2)_{av} = 1/2(H_{A-}^2)_{av} = 1/3(|H_A|^2)_{av} \\ (H_{Bz}^2)_{av} = 1/2(H_{B+}^2)_{av} = 1/2(H_{B-}^2)_{av} = 1/3(|H_B|^2)_{av}. \end{aligned} \quad [5]$$

It follows (19) that cross terms like $(H_{A(B)q}H_{A(B)p})_{av}$ and $(H_{Aq}H_{Bp})_{av}$ will vanish if $p \neq q$. When the fluctuating fields are not correlated we will also have $(H_{Aq}H_{Bq})_{av} = 0$.

We aim at obtaining the electron relaxation rates in the coupled systems as a combination of relaxation rates of uncoupled spins. At this point it is convenient to introduce the following definitions of the latter (19):

$$\begin{aligned} \tau_A^{-1} = 2/3\gamma_e^2\tau_v(|H_A|^2)_{av} \\ \text{and } \tau_B^{-1} = 2/3\gamma_e^2\tau_v(|H_B|^2)_{av}. \end{aligned} \quad [6]$$

Only one τ_v is used in (6) because this parameter is covariant with H_A and H_B .

The eigenfunctions of the static Hamiltonian [1] allow us to calculate the matrix elements of the time-dependent Hamiltonian [4] between the $|S'M_S\rangle$ of the coupled system. Then transition probabilities can be calculated by the formula (19)

$$W_{ij} = 2\tau_v([\langle i|\mathbf{H}(t)|j\rangle]^2)_{\text{av}} \quad \text{for } i \neq j. \quad [7]$$

The sum of transition probabilities from level i to all other levels gives the inverse lifetime of level i (τ_{ii}^{-1}). The W_{ij} and τ_{ii}^{-1} values (the latter taken with opposite sign as customary) are reported as supplementary material (Tables S1A–S4A) for the $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-1$, $\frac{1}{2}-\frac{3}{2}$, and 1–1 cases, respectively.

Then the adiabatic linewidths for each $i \rightarrow j$ transition can be calculated according to the formula (21)

$$(\tau^{\text{ad}})_{ij}^{-1} = \tau_v([\langle i|\mathbf{H}(t)|i\rangle - \langle j|\mathbf{H}(t)|j\rangle]^2)_{\text{av}}. \quad [8]$$

The corresponding values are also reported as supplementary material (Tables S1B–S4B). Finally, the total linewidth for each $i \rightarrow j$ transition is calculated by making use of the relationship

$$(\tau)_{ij}^{-1} = (\tau^{\text{ad}})_{ij}^{-1} + 1/2(\tau_{ii}^{-1} + \tau_{jj}^{-1}) \quad [9]$$

The τ_{ij}^{-1} values are reported in supplementary material (Tables S1C–S4C).

Calculation of Paramagnetic Nuclear Relaxation Enhancements

To derive the equations for the field dependence of the nuclear relaxation rates enhancements, according to the Kubo and Tomita treatment (14), we must evaluate expressions of the type

$$\left[\int_0^\infty f(r, \vartheta, \varphi) \langle i|S_p(t)|j\rangle \langle j|S_q(t)|i\rangle e^{\pm\omega t} dt \right]_{\text{sp av}}, \quad [10]$$

where $f(r, \vartheta, \varphi)$ is a function which describes the position of the proton in the laboratory coordinate frame, ω_l is the nucleus Larmor frequency, p and q stand for +, z, and – and i and j are eigenstates of Hamiltonian [1] (20). As the static Hamiltonian [1] is isotropic, the eigenfrequencies of the electron spin system do not depend on the orientation of the molecule. In this case a spherical average of $f(r, \vartheta, \varphi)$ can be taken. The result depends only on the components of the spherical spin operator tensor. The expression $\langle i|S_q(t)|j\rangle$ can be taken to be equal to $\langle i|S_q(0)|j\rangle e^{(i\omega_{ij}-1/\tau_e)t}$, where ω_{ij} is the eigenfrequency of Hamiltonian [1] (22–24). Omitting constants and before the spatial average in (10) can be performed, we must evaluate terms of the type

$$\langle i|S_p(0)|j\rangle \langle j|S_q(0)|i\rangle \int_0^\infty e^{i(\omega_{ij}\pm\omega)t - (t/\tau_e)} dt, \quad [11]$$

where τ_e is the electronic relaxation time, taken as the dominant correlation time for the electron–nucleus interaction.

The real part of the integral in [11] is equal to the familiar spectral density

$$\frac{\tau_e}{1 + (\omega_{ij} \pm \omega_l)^2 \tau_e^2}. \quad [12]$$

If the static Hamiltonian is given by [1] only the following products of expectation values will be different from zero

$$\langle i|S_+(0)|j\rangle \langle i|S_-(t)|j\rangle \quad [13]$$

$$\langle i|S_-(0)|j\rangle \langle i|S_+(t)|j\rangle \quad [14]$$

$$\langle i|S_z(0)|j\rangle \langle i|S_z(t)|j\rangle \quad [15]$$

Relaxation of the components S_+ and S_- occurs in the plane perpendicular to the direction of the static magnetic field. Therefore, for the spectral density terms originating from [13] or [14] the τ_e coefficients should be given by the corresponding $(\tau_2)_{ij}$. For the terms originating from [15] two cases can be considered with respect to τ_e . When $i = j$, then $\omega_{ij} = 0$ and τ_e coincides with the lifetime of level i , τ_{ii} . When $i \neq j$, at variance with a monometallic system, the expectation value $\langle i|S_z(0)|j\rangle$ can be different from zero. This occurs for the transitions between levels with the same $M_{S'}$ originating from different S' multiplets. In such case the $(\tau_2)_{ij}$ of the transition should be used as the correlation time. The distinction between the above two cases, however, is irrelevant when $J \gg$ Zeeman, as all terms involving transitions between J -split levels will be dispersed.

In summary, in the equations for nuclear relaxation rate enhancements all terms related to transitions within the same S' multiplet will have the corresponding $(\tau_2)_{ij}$ as a correlation time. All the so-called ω_l terms will contain as a correlation time the lifetime of the corresponding level, τ_{ii} . The level to be considered is identified by the indexes of the zero-valued frequency ω_{ii} .

RESULTS

Table 1 collects the total linewidths (τ_{ij}^{-1}) and inverse level lifetimes (τ_{ii}^{-1}) for the coupled S_A – S_B systems $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-1$, $\frac{1}{2}-\frac{3}{2}$, and 1–1, calculated as described under Theoretical Part.

Because of the same assumptions about fluctuating fields, the results for the spins $S_A = \frac{1}{2}$ and $S_B = \frac{1}{2}$ coincide with those of Freeman *et al.* (19) for two coupled nuclear spins when external fields are not correlated. For all spin pairs, the lifetimes of the levels and linewidths of transitions are expressed as linear combinations of the relaxation rates of uncoupled spins.

The τ_{ij}^{-1} and τ_{ii}^{-1} values of Table 1 constitute the full set

TABLE 1
Inverse Level Lifetimes, τ_{ii}^{-1} (Diagonal), and Total Transition Linewidths, τ_{ij}^{-1} (Off-Diagonal),
in Some Magnetic Exchange Coupled Systems

$S_A = \frac{1}{2}, S_B = \frac{1}{2}$				
	$\Psi_{1(4)}$		$\Psi_{1(4)}$	
	$\Psi_{2(3)}$			$\Psi_{2(3)}$
	$\Psi_{3(2)}$			
	$\Psi_{4(1)}$			
		$1/2R_A + 1/2R_B$		$3/4R_A + 3/4R_B$
		$3/4R_A + 3/4R_B$		$3/4R_A + 3/4R_B$
		$3/4R_A + 3/4R_B$		$3/4R_A + 3/4R_B$
		$R_A + R_B$		$3/4R_A + 3/4R_B$
$S_A = \frac{1}{2}, S_B = 1$				
		$\Psi_{1(6)}$	$\Psi_{2(5)}$	$\Psi_{3(4)}$
$\Psi_{1(6)}$		$1/2R_A + R_B$	$2/3R_A + 5/3R_B$	$5/6R_A + 4/3R_B$
$\Psi_{2(5)}$		$2/3R_A + 5/3R_B$	$13/18R_A + 17/9R_B$	$7/9R_A + 16/9R_B$
$\Psi_{3(4)}$		$5/6R_A + 4/3R_B$	$7/9R_A + 16/9R_B$	$13/18R_A + 14/9R_B$
$\Psi_{4(3)}$		$2/3R_A + 8/3R_B$	$13/18R_A + 14/9R_B$	$7/9R_A + 7/3R_B$
$\Psi_{5(2)}$		$5/6R_A + 7/3R_B$	$7/9R_A + 19/9R_B$	$13/18R_A + 20/9R_B$
$\Psi_{6(1)}$		$R_A + 3R_B$	$5/6R_A + 7/3R_B$	$2/3R_A + 8/3R_B$
$S_A = \frac{1}{2}, S_B = \frac{3}{2}$				
	$\Psi_{1(8)}$	$\Psi_{2(7)}$	$\Psi_{3(6)}$	$\Psi_{4(5)}$
$\Psi_{1(8)}$	$1/2R_A + 3/2R_B$	$5/8R_A + 21/8R_B$	$7/8R_A + 57/32R_B$	$3/4R_A + 15/4R_B$
$\Psi_{2(7)}$	$5/8R_A + 21/8R_B$	$11/16R_A + 51/16R_B$	$13/16R_A + 87/32R_B$	$9/8R_A + 15/4R_B$
$\Psi_{3(6)}$	$7/8R_A + 57/32R_B$	$13/16R_A + 87/32R_B$	$11/16R_A + 2R_B$	$3/4R_A + 117/32R_B$
$\Psi_{4(5)}$	$3/4R_A + 15/4R_B$	$9/8R_A + 15/4R_B$	$3/4R_A + 117/32R_B$	$3/4R_A + 15/4R_B$
$\Psi_{5(4)}$	$3/4R_A + 15/4R_B$	$9/8R_A + 15/4R_B$	$3/4R_A + 117/32R_B$	$3/4R_A + 15/4R_B$
$\Psi_{6(3)}$	$5/8R_A + 177/32R_B$	$11/16R_A + 147/32R_B$	$13/16R_A + 41/16R_B$	$3/4R_A + 117/32R_B$
$\Psi_{7(2)}$	$7/8R_A + 39/8R_B$	$13/16R_A + 69/16R_B$	$11/16R_A + 147/32R_B$	$9/8R_A + 15/4R_B$
$\Psi_{8(1)}$	$R_A + 6R_B$	$7/8R_A + 39/8R_B$	$5/8R_A + 177/32R_B$	$3/4R_A + 15/4R_B$
$S_A = 1, S_B = 1$				
	$\Psi_{1(9)}$	$\Psi_{2(8)}$	$\Psi_{3(7)}$	$\Psi_{4(6)}$
$\Psi_{1(9)}$	$R_A + R_B$	$3/2R_A + 3/2R_B$	$3/2R_A + 3/2R_B$	$15/8R_A + 15/8R_B$
$\Psi_{2(8)}$	$3/2R_A + 3/2R_B$	$7/4R_A + 7/4R_B$	$7/4R_A + 7/4R_B$	$15/8R_A + 15/8R_B$
$\Psi_{3(7)}$	$3/2R_A + 3/2R_B$	$7/4R_A + 7/4R_B$	$7/4R_A + 7/4R_B$	$15/8R_A + 15/8R_B$
$\Psi_{4(6)}$	$15/8R_A + 15/8R_B$	$15/8R_A + 15/8R_B$	$15/8R_A + 15/8R_B$	$7/4R_A + 7/4R_B$
Ψ_5	$2R_A + 2R_B$	$2R_A + 2R_B$	$2R_A + 2R_B$	$15/8R_A + 15/8R_B$
$\Psi_{6(4)}$	$15/8R_A + 15/8R_B$	$15/8R_A + 15/8R_B$	$15/8R_A + 15/8R_B$	$7/4R_A + 7/4R_B$
$\Psi_{7(3)}$	$5/2R_A + 5/2R_B$	$9/4R_A + 9/4R_B$	$9/4R_A + 9/4R_B$	$15/8R_A + 15/8R_B$
$\Psi_{8(2)}$	$5/2R_A + 5/2R_B$	$9/4R_A + 9/4R_B$	$9/4R_A + 9/4R_B$	$15/8R_A + 15/8R_B$
$\Psi_{9(1)}$	$3R_A + 3R_B$	$5/2R_A + 5/2R_B$	$5/2R_A + 5/2R_B$	$15/8R_A + 15/8R_B$

of correlation times needed in the nuclear relaxation equations for the coupled systems developed below.

We now examine the expected NMR properties of dimetallic systems experiencing isotropic exchange coupling as described by Hamiltonian [1] for $S_A = \frac{1}{2}$ and $S_B = \frac{1}{2}, 1$, and $\frac{3}{2}$. The $S_A = 1 - S_B = 1$ case is also examined.

The nuclear relaxation enhancements caused by dipolar coupling to an isolated electron spin multiplet, for instance S_A , when the latter is adequately described by the electronic Zeeman Hamiltonian

$$\mathbf{H} = g_e \mu_e \mathbf{S} \cdot \mathbf{B}_0 \quad [16]$$

are given by the well-known Solomon equation (25). For the case of electron relaxation being the dominant correlation time, the equation is

$$T_{1M}^{-1}(A) = \frac{2}{15} k_A S_A (S_A + 1) \times \left(3 \frac{\tau_1}{1 + \omega_j^2 \tau_1^2} + 7 \frac{\tau_2}{1 + \omega_s^2 \tau_2^2} \right), \quad [17]$$

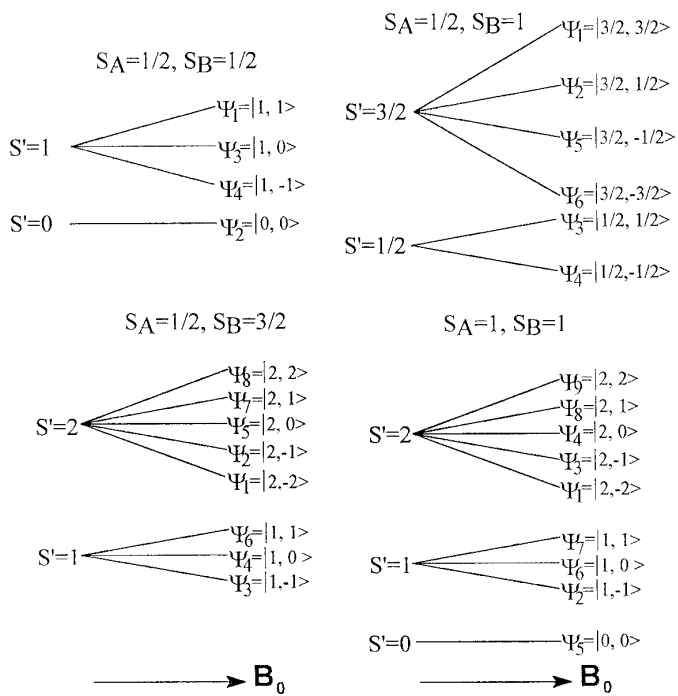


FIG. 1. Electronic spin energy levels for the dimetallic systems $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-\frac{3}{2}$, and $1-1$.

where the term in parentheses is the sum of two spectral densities, with τ_1 equal to the time constant for the relaxation of the S_z component and τ_2 that of the S_+ and S_- components (21). k is given by

$$k_A = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_I^2 g_e^2 \mu_e^2}{r_A^6}, \quad [18]$$

where μ_0 is the permeability of vacuum, γ_I is the nuclear magnetogyric ratio, g_e is the electron g factor, μ_e is the Bohr magneton, and r_A is the nucleus–electron distance. Analogous equations have been derived when the static electronic Hamiltonian contains zero field splitting, g anisotropy, and hyperfine coupling with the metal nucleus spin (17, 20, 26, 27). The approach can be that described by Kubo and Tomita (14) or by Redfield (16). Using the same approaches, the effect of Hamiltonian [1] can be also introduced. An equation for the $S_A = \frac{1}{2}$ and $S_B = \frac{1}{2}$ case has been already reported (17).

The electronic spin levels for the dimetallic systems considered here and described by Hamiltonian [1] are sketched in Fig. 1. In the following, electronic spin levels and transitions will be labeled according to Fig. 1.

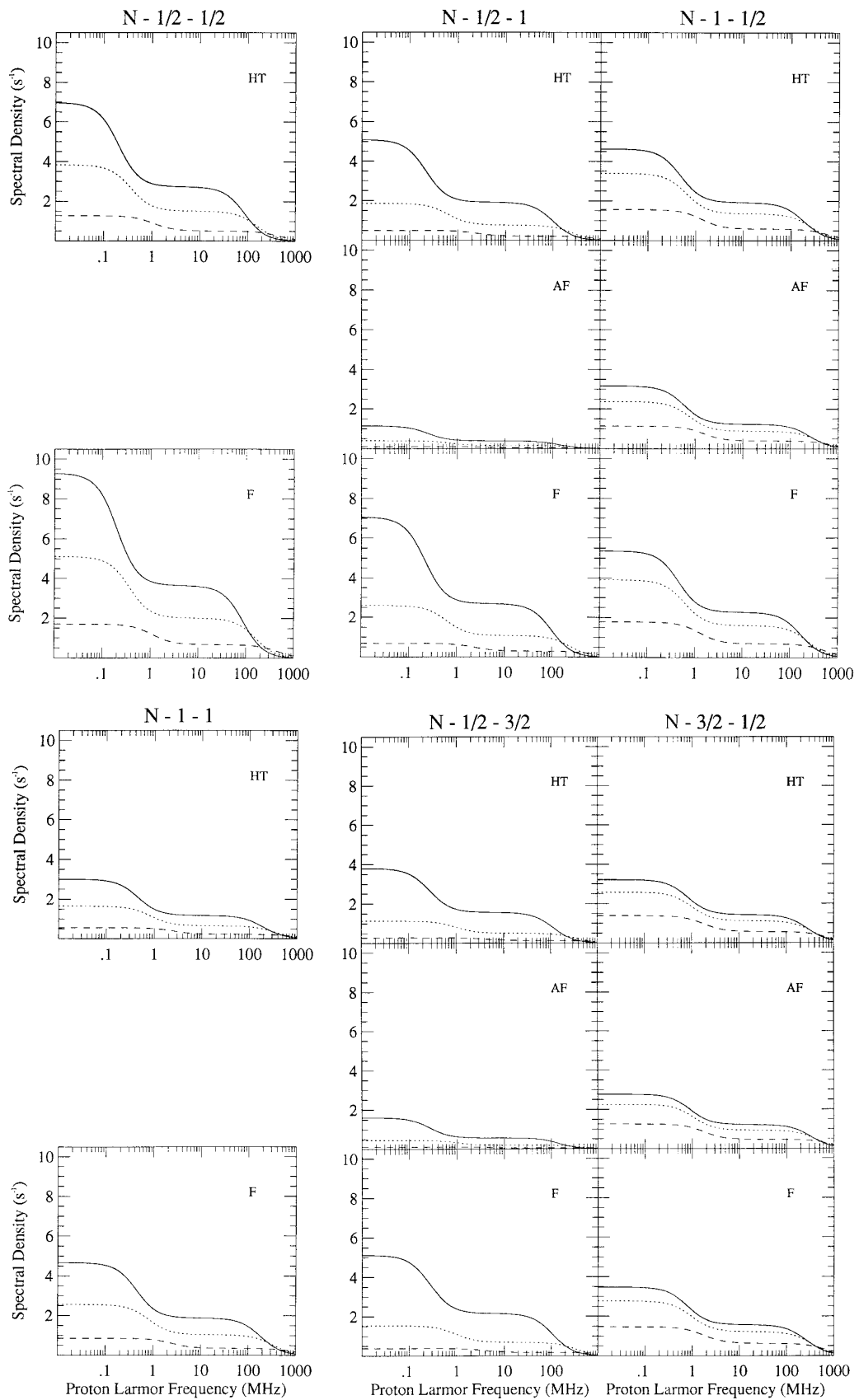
The contribution to the enhancement given by each metal ion in the pair is calculated separately. If the nucleus interacts with both metal ions the total effect is the sum of the effects.

The equations for the various cases, calculated as described under Theoretical Part, are reported in the Appendix (Eqs. [A1]–[A6]). The $\frac{2}{15}$ coefficient in front of all equations is the same coefficient appearing in Eq. [17], so that the sum of the F -containing terms, multiplied by a further coefficient, can be directly compared with the sum of the spectral densities appearing in parentheses in Eq. [17].

Equations [A1]–[A6], with the correlation times reported in Table 1, can be used to calculate NMRD profiles. Prediction of the latter without a theoretical treatment like the present one appears to be not a trivial task, as the NMRD profiles turn out to depend on (i) the relative values of the electronic relaxation rates of metals A and B when isolated, R_A and R_B ; (ii) the identity of the metal (A or B) with which the nucleus predominantly interacts; (iii) the relative magnitude of $|J|$ and the thermal energy, kT ; and (iv) the nature (ferro- or antiferro-) of the magnetic coupling between the two metals, in the case of $|J| \gg kT$.

Figure 2 shows the calculated NMRD profiles for all cases considered here. With the obvious exception of the $\frac{1}{2}-\frac{1}{2}$ and $1-1$ cases, for which a strong antiferromagnetic coupling ($J \gg kT$) yields a diamagnetic system, three situations are considered: the high temperature (HT) limit and the $|J| \gg kT$ limits for both $J > 0$ (AF) and $J < 0$ (F). The figure thus consists of two panels each for the $\frac{1}{2}-\frac{1}{2}$ and $1-1$ cases and six panels each for the $\frac{1}{2}-1$ and $\frac{1}{2}-\frac{3}{2}$ cases. In fact, the latter two cases involve $S_A \neq S_B$, and two sets of calculations have been performed for the nucleus, N, interacting with either one of the two spins. In each panel, three profiles calculated with the appropriate equations are shown. In all cases and without loss of generality, the spin interacting with the nucleus was assumed to have an electronic relaxation rate $R = 10^9 \text{ s}^{-1}$. The full line refers to the case of the second spin having a relaxation rate of 10^8 s^{-1} , the dotted line to the case of the second spin having the same relaxation rate as the first spin (10^9 s^{-1}), and the dashed line to the case of the second spin having a relaxation rate five times faster than the first spin ($5 \times 10^9 \text{ s}^{-1}$). For convenience, the NMRD profiles are reported as spectral densities, normalized by division by the $S(S+1)$ value of the spin interacting with the nucleus. In this way, an uncoupled spin would give the usual low field reference value of 10 and a spectral density of 3 at field values intermediate between the $\omega_S \tau$ and the $\omega_I \tau$ dispersions (Solomon equation, Eq. [17] with $\tau_1 = \tau_2 = \tau$).

It appears that in all cases the profiles at low field are lower than the Solomon profiles. This depends on the reduced availability of electronic transitions for nuclear relaxation, as the transitions involving J -split levels are dispersed. Another general feature is the higher NMRD profile in the $J < 0$ (F) case with respect to the $J > 0$ (AF) case, with the high temperature limit profile being intermediate. This is



accounted for intuitively by the larger paramagnetism of the ground state in the former case.

The dependence of the NMRD intensity, for a nucleus interacting with one spin, on the electronic relaxation rate of the other spin is not the same for the various cases. In general, the effect is less pronounced when the spin interacting with the nucleus is the larger of the two, and more pronounced when it is the smaller. The cases of equal spins are intermediate.

A most striking feature, however, is the variability of the ratio of the low field to the intermediate field plateaus. Such ratio is 10/3 in the Solomon case, and would be 10/3 in the present cases if the τ_{ij} and τ_{ii} values were equal. Our calculations of the individual τ_{ij} and τ_{ii} values show that these values may differ one from another, depending also on the relative values of R_A and R_B .

Furthermore, the two dispersions are (i) not strictly Lorentzian, as they are made up of sums of Lorentzians with different τ values, and (ii) not spaced in frequency by the ω_S/ω_I ratio, as in the Solomon case when $\tau_1 = \tau_2$ (Eq. [17]). However, inspection of the relevant values in Table 1 shows that the τ_{ij} values never differ from one another by more than a factor of 4, and the same is true for the τ_{ii} values. Under these conditions, it is well known that a sum of Lorentzians is well approximated by a single Lorentzian having a reciprocal τ value equal to the weighted average of the individual reciprocal τ values.

The average effective τ values calculated for the low field and high field dispersions (τ_2 and τ_1 , respectively) from the individual τ_{ij} and τ_{ii} values, respectively, are shown in Table 2. Practically identical values are obtained by actually fitting the calculated profiles of Fig. 2 using two effective τ values and an effective Solomon equation equal to Eq. [17] but multiplied by a further C_A coefficient. The C_A values obtained from the fit are also very close to the values of $\frac{1}{2}$, $\frac{11}{27}$, $\frac{3}{8}$, and $\frac{1}{2}$ appearing in Eqs. [A1]–[A6] in the cases $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-1$, $\frac{1}{2}-\frac{3}{2}$, and $1-1$, respectively, when the nucleus is interacting with spin A, in the HT limit. Likewise, C_B coefficients very close to the $\frac{1}{2}$, $\frac{7}{9}$, $\frac{7}{8}$, and $\frac{1}{2}$ values of Eqs. [A1]–[A6] are obtained when the nucleus is interacting with spin B. Analogously, the fits in the AF and F low temperature limits yield C_A and C_B coefficients very close to those that can be calculated from Eqs. [A1]–[A6] in the same limits.

DISCUSSION

The main result of this work is that nuclear relaxation in coupled systems can always be treated as originating from

a single electron spin system characterized by a single longitudinal (τ_1) and transverse (τ_2) electron relaxation time. Indeed, each τ_1^{-1} and τ_2^{-1} value of Table 2 is independent of whether the nucleus senses metal A or metal B, since such average values characterize the coupled system as a whole, as a result of condition [2]. In other words, the two metal ions have the same average relaxation time. Furthermore, when R_A and R_B differ by an order of magnitude or more, the average value is closer to the larger rather than to the smaller R value.

When $R_A \cong R_B$, and $S_A = S_B = \frac{1}{2}$, the average τ_1^{-1} and τ_2^{-1} values are, respectively, equal to, and 50% larger than, the value of the uncoupled system. For $S_A = S_B = 1$, both τ_1^{-1} and τ_2^{-1} become larger than that of the uncoupled system.

For different spins, the relaxation rate of the smaller spin is multiplied by a factor between 0.5 and 1, and that of the larger by a factor between 1 and 4. The factors multiplying R_A and R_B for the calculation of τ_1^{-1} are in any case smaller than the corresponding factors for the calculation of τ_2^{-1} . In all cases, the small spin contributes to the average τ_1^{-1} and τ_2^{-1} values less than the large spin.

Figure 3 shows in graphical form how much the effective τ_1 and τ_2 values in the coupled systems differ from the R_A and R_B values in a variety of circumstances. In all cases, it is assumed that the electron relaxation rate of one spin (R_B or R_A) is 10^9 s^{-1} , and the electron relaxation rate of the other spin (R_A or R_B) varies from 10^7 to 10^{12} s^{-1} . The six panels refer to all the different possibilities for a nucleus to interact with one of the spin pairs $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-1$, $\frac{1}{2}-\frac{3}{2}$, $1-1$. The full lines are calculated in the HT limit, the dotted and dashed lines in the AF and F limits, respectively. The $\tau^{-1} = 10^9 \text{ s}^{-1}$ and $\tau^{-1} = R_A$ (R_B) lines are also shown.

As already noted, when the R values differ much from one another, the effective τ_1^{-1} and τ_2^{-1} values are relatively close to the larger R . However, the detailed behavior is different. For instance, in the $1-1$ case τ_2^{-1} and τ_1^{-1} are always larger than the larger R , while in the $\frac{1}{2}-\frac{1}{2}$ case the opposite is true, except when R_A and R_B are equal or similar within a factor 3. In the cases of unequal spins, with sizably different R values, when the larger R value is associated with the ion with larger S , τ^{-1} is sizably larger than the larger value. On the contrary, if the larger R value is associated with the ion with smaller S , τ^{-1} is close to, but slightly smaller than, R .

In summary, Table 2 allows experimentalists to fit NMRD data of coupled systems by using the R_A and R_B values of

FIG. 2. NMRD profiles (spectral densities, normalized to 10 for the Solomon case, as a function of the proton Larmor frequency) for the $\frac{1}{2}-\frac{1}{2}$, $\frac{1}{2}-1$, $\frac{1}{2}-\frac{3}{2}$, and $1-1$ systems. In each system, the HT, F, and AF limits are considered (see text) for $R_B < R_A$ ($R_B = 10^8 \text{ s}^{-1}$, solid line), $R_B = R_A$ ($R_B = 10^9 \text{ s}^{-1}$, dotted line), and $R_B > R_A$ ($R_B = 5 \times 10^9 \text{ s}^{-1}$, dashed line). Calculations are performed for the nucleus, N, interacting with either one of the two spins.

TABLE 2
Effective Electron Relaxation Rates for J -Coupled Systems ($\frac{1}{2}-\frac{1}{2}$; $\frac{1}{2}-1$; $\frac{1}{2}-\frac{3}{2}$; and $1-1$) in the HT, AT, and F Limits^a

		N- S_A			N- S_B		
		HT	AF	F	HT	AF	F
$S_A = \frac{1}{2}, S_B = \frac{1}{2}$							
τ_1^{-1}	$1/2R_A + 1/2R_B$	Diamagnetic state	$1/2R_A + 1/2R_B$	$1/2R_A + 1/2R_B$	Diamagnetic state	$1/2R_A + 1/2R_B$	$1/2R_A + 1/2R_B$
τ_2^{-1}	$3/4R_A + 3/4R_B$		$3/4R_A + 3/4R_B$	$3/4R_A + 3/4R_B$		$3/4R_A + 3/4R_B$	$3/4R_A + 3/4R_B$
$S_A = \frac{1}{2}, S_B = 1$							
τ_1^{-1}	$107/198R_A + 112/99R_B$	$13/18R_A + 14/9R_B$	$47/90R_A + 49/45R_B$	$73/126R_A + 77/63R_B$	$13/18R_A + 14/9R_B$	$47/90R_A + 49/45R_B$	$47/90R_A + 49/45R_B$
τ_2^{-1}	$71/99R_A + 187/99R_B$	$7/9R_A + 7/3R_B$	$32/45R_A + 83/45R_B$	$46/63R_A + 125/63R_B$	$7/9R_A + 7/3R_B$	$32/45R_A + 83/45R_B$	$32/45R_A + 83/45R_B$
$S_A = \frac{1}{2}, S_B = \frac{3}{2}$							
τ_1^{-1}	$9/16R_A + 179/96R_B$	$11/16R_A + 2R_B$	$43/80R_A + 147/80R_B$	$331/560R_A + 2123/1120R_B$	$11/16R_A + 2R_B$	$43/80R_A + 147/80R_B$	$43/80R_A + 147/80R_B$
τ_2^{-1}	$43/48R_A + 215/64R_B$	$3/4R_A + 117/32R_B$	$37/40R_A + 33/10R_B$	$69/80R_A + 7677/2240R_B$	$3/4R_A + 117/32R_B$	$37/40R_A + 33/10R_B$	$37/40R_A + 33/10R_B$
$S_A = 1, S_B = 1$							
τ_1^{-1}	$5/4R_A + 5/4R_B$	Diamagnetic state	$23/20R_A + 23/20R_B$	$5/4R_A + 5/4R_B$	Diamagnetic state	$23/20R_A + 23/20R_B$	$23/20R_A + 23/20R_B$
τ_2^{-1}	$7/4R_A + 7/4R_B$		$69/40R_A + 69/40R_B$	$7/4R_A + 7/4R_B$		$69/40R_A + 69/40R_B$	$69/40R_A + 69/40R_B$

^a Calculations are performed for the nucleus, N, interacting with either one of the two spins.

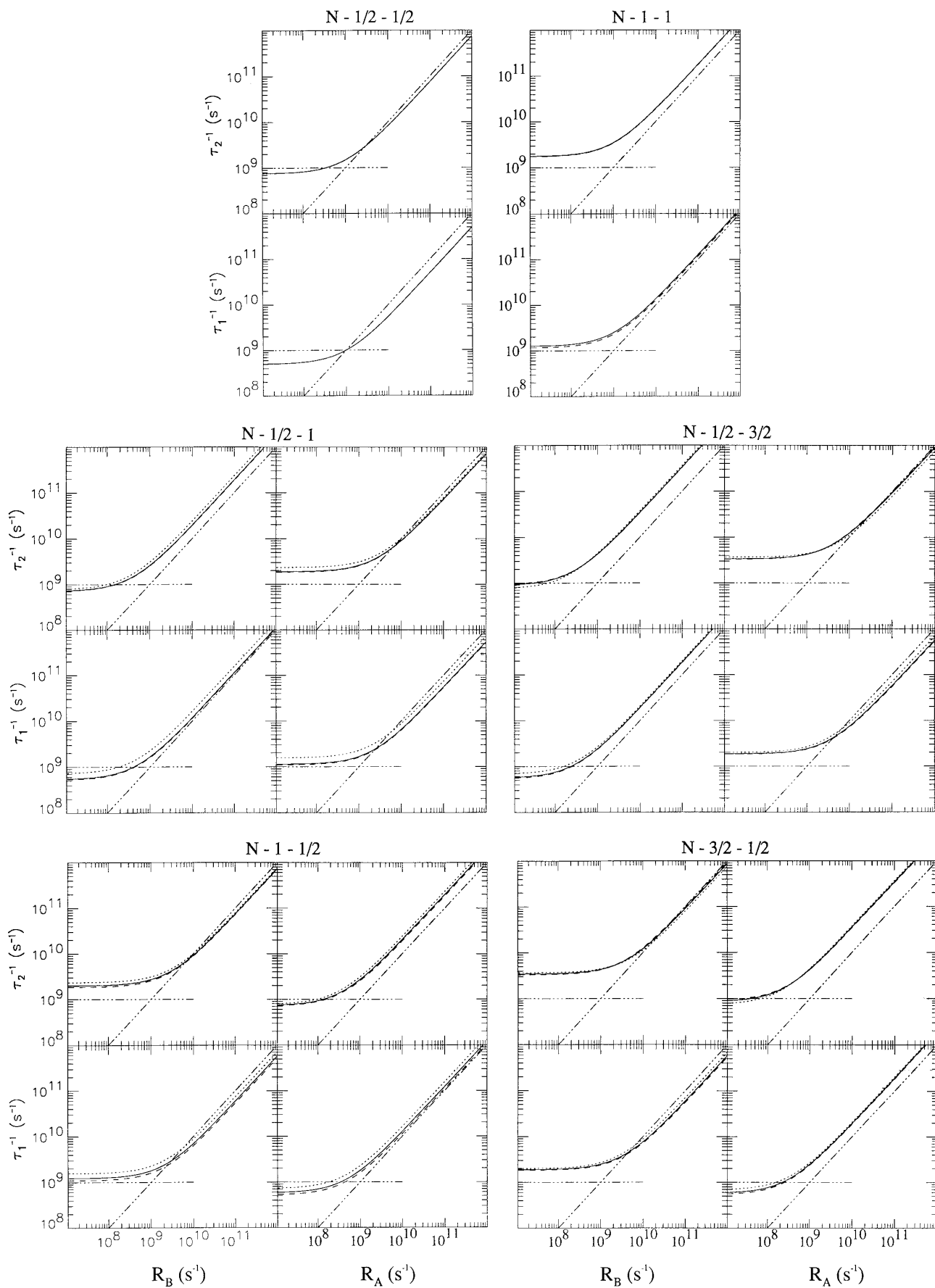
the uncoupled systems as the only unknowns. Of course, this only holds in the starting assumption that no additional relaxation mechanisms are operative in the coupled systems. τ_1^{-1} and τ_2^{-1} larger than predicted should reveal the presence of additional relaxation mechanisms.

Experimental data on τ_1 are available for a copper dimer in Cu_2Cu_2 superoxide dismutase (28) where $J = 26 \text{ cm}^{-1}$ (29), as well as for the native Cu_2Zn_2 superoxide dismutase system (28). Assuming $R_A = R_B$, no change in τ_1 should be expected, while a factor two decrease in nuclear relaxation should be observed due to the $\frac{1}{2}$ coefficient in Eq. [A1]. The τ_1 values have been estimated with a modified Solomon equation that takes into account the effect of the coupling of the unpaired electron of copper with the copper $I = \frac{3}{2}$ nucleus (20, 26), as well as the possible effects of zero field splitting (ZFS) for $S > \frac{1}{2}$ ions (20, 23). The τ_1 values actually increase from about 3 to 4 ns on passing from the uncoupled to the coupled system, while the best fit value of the coefficient is 0.57 (28). Both parameters are thus in substantially good agreement with the expectations. τ_2 values cannot be obtained from NMRD measurements in this case because the low field inflections of the NMRD profiles are determined by the value of the hyperfine coupling be-

tween the unpaired electron on copper and the copper $I = \frac{3}{2}$ nucleus. However, it is well known that in other copper (II) dimers the EPR linewidths are larger than in the corresponding uncoupled systems (30). The present prediction of a 50% increase in linewidth is in agreement with these observations. Finally, in several copper-copper dimers relatively sharp ^1H NMR lines are observed (31-34). It has been suggested that the such sharp lines arise from a sizable shortening of the electronic relaxation times of the copper ions with respect to the uncoupled situation (33, 34), beyond that predicted from the present treatment. In these cases, usually characterized by relatively short metal-metal distances, modulation of ZFS of the dimer $S' = 1$ state may be an additional electronic relaxation mechanism (34).

Experimental data on τ_1 are also available for the Cu_2Co_2 derivative of superoxide dismutase, which displays a J value of 17 cm^{-1} (35). The NMR data, collected over a range of magnetic fields from 60 to 400 MHz, refer to protein protons sensing either the copper or the cobalt ion (36). The R_{Cu} and R_{Co} data obtained on suitable uncoupled derivatives are 5×10^8 and $1 \times 10^{11} \text{ s}^{-1}$, respectively (36). This is thus a typical case of one ion relaxing much faster than the other ion. From Table 2, in the high temperature approximation,

FIG. 3. Effective correlation rates for nuclear relaxation, τ_2^{-1} and τ_1^{-1} , as a function of the electron relaxation rate of one spin, that of the other spin being equal to 10^9 s^{-1} . The electron relaxation rate of the spin interacting with the nucleus is labeled R_A , while that of the second spin is labeled R_B . Solid, dotted, and dashed lines refer to the HT, AF, and F limits, respectively (see text). Calculations are performed for the nucleus, N, interacting with either one of the two spins.



τ_1^{-1} should be equal to $\frac{9}{16} R_{\text{Cu}} + \frac{179}{96} R_{\text{Co}}$, i.e., about twice R_{Co} , or $2 \times 10^{11} \text{ s}^{-1}$. The experimental τ_1^{-1} value ranges between 1 and $2 \times 10^{11} \text{ s}^{-1}$ depending on whether it is estimated from the relaxation properties of the protons close to the copper or to the cobalt ion. Again, the agreement with prediction is very good. In particular, the more than two orders of magnitude decrease in the electron relaxation time of copper, and even the factor two decrease in the electron relaxation time of cobalt, are observed as predicted.

CONCLUDING REMARKS

The perception that the electronic relaxation times of uncoupled metal ions change upon magnetic coupling is here put on quantitative basis for some idealized cases. The presence of ZFS has not been taken into consideration because of the loss of generality, in that information on ZFS rarely is available. If ZFS parameters are known, then it is easy to include them in the calculations within the present frame (20). While a perturbative approach was available for weak coupling (4), no attempt is available in the literature to relate the electronic relaxation times of a single ion with that of the same ion in a strongly magnetic coupled dimer. Here we have calculated the transition probabilities between levels arising from magnetic coupling and the indetermination of the transitions. Many correlation times are thus obtained, which can be of little help to spectroscopists. Since we are interested particularly in the effects on nuclei which are coupled with electrons in magnetic coupled systems, we have calculated the nuclear relaxation rates at any magnetic field. Then, from the latter calculated values we have extracted a pair of effective electronic correlation times which are the ones NMR spectroscopists want. In this way a simple equation similar to the well-known Solomon equation can be used for dimetallic systems.

A final remark is that it is possible that establishing magnetic coupling provides further electron relaxation mechanisms, and that the average τ_1 and τ_2 values are much smaller than those reported in Table 2. However, the consequences on nuclear relaxation for nuclei interacting with the A or B spins, given in Eqs. [A1]–[A6], are still fully valid.

APPENDIX

Equations for Nuclear Relaxation in Some Magnetic Exchange Coupled Systems

The following equations are generally valid under conditions [1]–[4] described under Theoretical Part. In the equations, τ_{ij}^{-1} represents the total linewidth (in radians per second) of the transition between levels i and j in the coupled system, whereas τ_{ii} represents the lifetime of level i . The τ_{ij}^{-1} and τ_{ii}^{-1} values are reported in Table 1 for the various

cases. The labeling of electron spin levels and transitions is shown in Fig. 1. The $\tau_{ij}/(1 + \omega_{ij}^2 \tau_{ij}^2)$ dispersions corresponding to transitions between electronic levels split by J are omitted because they are quenched in the chosen limit $|J|/\hbar \gg \tau_{ij}^{-1}$.

$$S_A = \frac{1}{2} \text{ and } S_B = \frac{1}{2}$$

$$\begin{aligned} T_{1M}^{-1}(A) &= T_{1M}^{-1}(B) \\ &= \frac{2}{15} k_{A(B)} S_A (S_A + 1) \\ &\quad \times \frac{1}{2} \frac{4F_1 e^{-E_1/kT}}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}}, \end{aligned} \quad [\text{A1}]$$

where

$$\begin{aligned} F_1 &= \frac{3}{2} \frac{\tau_{11}}{1 + \omega_I^2 \tau_{11}^2} + \frac{3}{2} \frac{\tau_{44}}{1 + \omega_I^2 \tau_{44}^2} \\ &\quad + \frac{7}{2} \frac{\tau_{13}}{1 + \omega_{13}^2 \tau_{13}^2} + \frac{7}{2} \frac{\tau_{34}}{1 + \omega_{34}^2 \tau_{34}^2}, \end{aligned}$$

and $E_{S'}$ refers to the energy of the spin state S' . All four spectral densities in F_1 are multiplied by the same exponential, as the individual Zeeman energy contribution can be neglected in accordance with the condition that the exchange coupling energy $|J|$ is much larger than the difference in the Zeeman energies. Note that the nuclear relaxation enhancements caused by the two metal ions are identical under any condition, even when the two metal ions are markedly different and have very different electronic relaxation times when isolated. This equation reduces to the equation previously proposed (17) for $\tau_{13} = \tau_{34} = \tau_{11} = \tau_{44} = \tau$.

$$S_A = \frac{1}{2} \text{ and } S_B = 1$$

$$\begin{aligned} T_{1M}^{-1}(A) &= \frac{2}{15} k_A S_A (S_A + 1) \\ &\quad \times \frac{11}{27} \left[\frac{6(F_{1/2}^A e^{-E_{1/2}/kT} + F_{3/2}^A e^{-E_{3/2}/kT})}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}} \right], \end{aligned} \quad [\text{A2}]$$

where

$$F_{1/2}^A = \frac{3}{11} \frac{\tau_{33(44)}}{1 + \omega_I^2 \tau_{33(44)}^2} + \frac{7}{11} \frac{\tau_{34}}{1 + \omega_{34}^2 \tau_{34}^2}$$

and

$$F_{3/2}^A = \frac{27}{11} \frac{\tau_{11(66)}}{1 + \omega_I^2 \tau_{11(66)}^2} + \frac{3}{11} \frac{\tau_{22(55)}}{1 + \omega_I^2 \tau_{22(55)}^2} + \frac{21}{11} \frac{\tau_{12}}{1 + \omega_{12}^2 \tau_{12}^2} + \frac{21}{11} \frac{\tau_{56}}{1 + \omega_{56}^2 \tau_{56}^2} + \frac{28}{11} \frac{\tau_{25}}{1 + \omega_{25}^2 \tau_{25}^2}.$$

$F_{1/2}^A$ and $F_{3/2}^A$ refer to the spectral densities originating from the $S' = \frac{1}{2}$ or $\frac{3}{2}$, respectively. The ground state can be either the $E_{1/2}$ or the $E_{3/2}$ level according to whether $J > 0$ (antiferromagnetic coupling) or $J < 0$ (ferromagnetic coupling).

$$T_{1M}^{-1}(\mathbf{B}) = \frac{2}{15} k_B S_B (S_B + 1) \times \frac{7}{9} \left[\frac{6(F_{1/2}^B e^{-E_{1/2}/kT} + F_{3/2}^B e^{-E_{3/2}/kT})}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}} \right], \quad [\text{A3}]$$

where

$$F_{1/2}^B = \frac{6}{7} \frac{\tau_{33(44)}}{1 + \omega_I^2 \tau_{33(44)}^2} + 2 \frac{\tau_{34}}{1 + \omega_{34}^2 \tau_{34}^2}$$

and

$$F_{3/2}^B = \frac{27}{14} \frac{\tau_{11(66)}}{1 + \omega_I^2 \tau_{11(66)}^2} + \frac{3}{14} \frac{\tau_{22(55)}}{1 + \omega_I^2 \tau_{22(55)}^2} + \frac{3}{2} \frac{\tau_{12}}{1 + \omega_{12}^2 \tau_{12}^2} + \frac{3}{2} \frac{\tau_{56}}{1 + \omega_{56}^2 \tau_{56}^2} + 2 \frac{\tau_{25}}{1 + \omega_{25}^2 \tau_{25}^2}.$$

$$S_A = \frac{1}{2} \text{ and } S_B = \frac{3}{2}$$

$$T_{1M}^{-1}(\mathbf{A}) = \frac{2}{15} k_A S_A (S_A + 1) \times \frac{3}{8} \left[\frac{8(F_1^A e^{-E_1/kT} + F_2^A e^{-E_2/kT})}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}} \right], \quad [\text{A4}]$$

where

$$F_1^A = \frac{1}{2} \frac{\tau_{33(66)}}{1 + \omega_I^2 \tau_{33(66)}^2} + \frac{7}{12} \frac{\tau_{43}}{1 + \omega_{43}^2 \tau_{43}^2} + \frac{7}{12} \frac{\tau_{64}}{1 + \omega_{64}^2 \tau_{64}^2}$$

$$F_2^A = 2 \frac{\tau_{11(88)}}{1 + \omega_I^2 \tau_{11(88)}^2} + \frac{1}{2} \frac{\tau_{22(77)}}{1 + \omega_I^2 \tau_{22(77)}^2} + \frac{7}{6} \frac{\tau_{87}}{1 + \omega_{87}^2 \tau_{87}^2} + \frac{7}{6} \frac{\tau_{21}}{1 + \omega_{21}^2 \tau_{21}^2} + \frac{7}{4} \frac{\tau_{52}}{1 + \omega_{52}^2 \tau_{52}^2} + \frac{7}{4} \frac{\tau_{75}}{1 + \omega_{75}^2 \tau_{75}^2}$$

and

$$T_{1M}^{-1}(\mathbf{B}) = \frac{2}{15} k_B S_B (S_B + 1) \times \frac{7}{8} \left[\frac{8(F_1^B e^{-E_1/kT} + F_2^B e^{-E_2/kT})}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}} \right], \quad [\text{A5}]$$

where

$$F_1^B = \frac{15}{14} \frac{\tau_{33(66)}}{1 + \omega_I^2 \tau_{33(66)}^2} + \frac{5}{4} \frac{\tau_{43}}{1 + \omega_{43}^2 \tau_{43}^2} + \frac{5}{4} \frac{\tau_{64}}{1 + \omega_{64}^2 \tau_{64}^2}$$

$$F_2^B = \frac{54}{35} \frac{\tau_{11(88)}}{1 + \omega_I^2 \tau_{11(88)}^2} + \frac{27}{70} \frac{\tau_{22(77)}}{1 + \omega_I^2 \tau_{22(77)}^2} + \frac{9}{10} \frac{\tau_{87}}{1 + \omega_{87}^2 \tau_{87}^2} + \frac{9}{10} \frac{\tau_{21}}{1 + \omega_{21}^2 \tau_{21}^2} + \frac{27}{20} \frac{\tau_{52}}{1 + \omega_{52}^2 \tau_{52}^2} + \frac{27}{20} \frac{\tau_{75}}{1 + \omega_{75}^2 \tau_{75}^2}.$$

$$S_A = 1 \text{ and } S_B = 1$$

$$T_{1M}^{-1}(\mathbf{A}) = T_{1M}^{-1}(\mathbf{B}) = \frac{2}{15} k_{A(B)} S_A (S_A + 1) \times \frac{1}{2} \left[\frac{9(F_1 e^{-E_1/kT} + F_2 e^{-E_2/kT})}{\sum_{S'} (2S' + 1) e^{-E_{S'}/kT}} \right], \quad [\text{A6}]$$

where

$$F_1 = \frac{1}{2} \frac{\tau_{22(77)}}{1 + \omega_I^2 \tau_{22(77)}^2} + \frac{7}{12} \frac{\tau_{62}}{1 + \omega_{62}^2 \tau_{62}^2} + \frac{7}{12} \frac{\tau_{76}}{1 + \omega_{76}^2 \tau_{76}^2}$$

and

$$F_2 = 2 \frac{\tau_{11(99)}}{1 + \omega_I^2 \tau_{11(99)}^2} + \frac{1}{2} \frac{\tau_{33(88)}}{1 + \omega_I^2 \tau_{33(88)}^2} + \frac{7}{6} \frac{\tau_{31}}{1 + \omega_{31}^2 \tau_{31}^2} + \frac{7}{4} \frac{\tau_{43}}{1 + \omega_{43}^2 \tau_{43}^2} + \frac{7}{4} \frac{\tau_{84}}{1 + \omega_{84}^2 \tau_{84}^2} + \frac{7}{6} \frac{\tau_{98}}{1 + \omega_{98}^2 \tau_{98}^2}.$$

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