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Communication

Cross relaxation in nitroxide spin labels

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ABSTRACT

Cross relaxation, and m_I -dependence of the intrinsic electron spin-lattice relaxation rate W_e , are incorporated explicitly into the rate equations for the electron-spin population differences that govern the saturation behaviour of ^{14}N - and ^{15}N -nitroxide spin labels. Both prove important in spin-label EPR and ELDOR, particularly for saturation recovery studies. Neither for saturation recovery, nor for CW-saturation EPR and CW-ELDOR, can cross relaxation be described simply by increasing the value of W_e , the intrinsic spin-lattice relaxation rate. Independence of the saturation recovery rates from the hyperfine line pumped or observed follows directly from solution of the rate equations including cross relaxation, even when the intrinsic spin-lattice relaxation rate W_e is m_I -dependent.

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1. Introduction

Use of saturation recovery (SR) techniques in spin-label EPR is currently increasing and is likely to continue to grow (see, e.g., Refs. [1–5]). Particularly promising, for instance, is the use of SR-EPR to study molecular mobility in biological systems [4,6,7], and of T_1 -exchange spectroscopy to detect major conformational changes in proteins [2]. Indeed, both SR-EPR and saturation recovery electron-electron double resonance (SR-ELDOR) are sure of a bright future in the application of site-directed spin labelling [5].

Rate equations for the electron-spin population differences have proved a powerful and general means to analyse saturation recovery EPR experiments [1,2,8–13]. However, treatments of SR-EPR and SR-ELDOR by rate equations almost invariably ignore cross relaxation, although explicit calculation for electron-nuclear dipolar (END) interactions shows that cross relaxation makes an important contribution to the rate of saturation recovery [14,15]. Here I refer to cross relaxation as defined in Refs. [16,17], i.e., electron spin flips arising from the flip-flop and flop-flop non-secular END terms (see, e.g., Fig. 1). With two notable exceptions [18,19], cross relaxation arising from END also is largely ignored in treatments of both CW-saturation and CW-ELDOR (see, e.g., Refs. [20,21], and also Ref. [22] and references therein).

An associated issue is the dependence of the intrinsic electron spin-lattice relaxation rate on nitrogen nuclear hyperfine manifold (see, e.g. 16,17). Experimentally, Percival and Hyde [23] find no dependence of the recovery rate in long-pulse SR-EPR on nuclear magnetic quantum number m_I , for both ^{14}N - and ^{15}N -nitroxides. In consequence, a constant electron relaxation rate W_e , independent of m_I , has been assumed in rate equations used subsequently to analyse SR-EPR and SR-ELDOR of nitroxide spin labels [1,8–11]. Robinson et al. [24] resolved this apparent contradiction by quantum statistical calculations of the quantity observable in an SR-EPR experiment, namely the ensemble average of the expectation value for the z-magnetisation of the electron spins in the coupled system. In fact, lack of dependence on m_I is already inherent in the earlier treatments by rate equations [8–12], because solutions for the electron-spin population differences are sums of exponentials with rate constants that are independent of initial conditions, and hence of which hyperfine manifold is pumped or observed. However, the implications of this general result were hitherto obscured in these earlier treatments by assuming *a priori* that spin-lattice relaxation rates are equal.

Here, I include cross-relaxation, and the m_I -dependence of intrinsic electron spin-lattice relaxation, explicitly in rate equations for the electron-spin population differences in saturation recovery EPR and ELDOR, in progressive-saturation CW-EPR, and in CW-ELDOR. I treat both ^{14}N - and ^{15}N -nitroxide spin labels. For the latter, the results are totally in agreement with those of Ref. [24]. These results are important for analysing spin-label rotational mobility by saturation recovery techniques, for determining both accessibility to paramagnetic relaxants in site-directed spin

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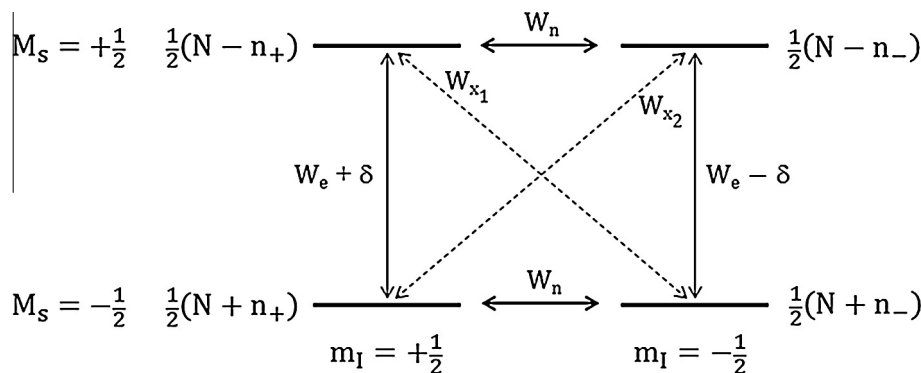


Fig. 1. Energy levels, spin populations and transitions for a ^{15}N -nitroxide spin label ($S = \frac{1}{2}, I = \frac{1}{2}$) in a magnetic field. Spin states are labeled by their electron and nuclear magnetic quantum numbers, M_S and m_I respectively. The total spin population N is the same in both hyperfine states. Spin-lattice relaxation pathways are given by solid arrows. Corresponding transition probabilities per unit time are: $W_e \pm \delta$ for electron transitions and W_n for nuclear transitions. Cross relaxation corresponds to simultaneous electron and nuclear transitions (dashed arrows), and the transition probabilities are: W_{x_1} and W_{x_2} for $\Delta M_S = \pm 1, \Delta m_I = \pm 1$ and $\Delta M_S = \pm 1, \Delta m_I = \mp 1$, respectively.

labelling and translational mobility/collisional kinetics by CW-EPR (by setting the time-scale), and quite generally in relating relaxation parameters to molecular dynamics. Treatment by rate equations has the advantage that, in addition to rate constants, amplitudes of the saturation recovery components for explicit transitions pumped and observed emerge automatically [8,12]. As is well known, population analysis applies only to spin-lattice relaxation and cannot be applied to the secular part of transverse relaxation, but this does not concern us here.

2. Transition probabilities for electron, nuclear and cross relaxation

I begin by listing the transitions contributing to nitroxide relaxation that arise from modulation of the Zeeman and hyperfine anisotropies, and their dependence on the nitrogen nuclear hyperfine state (see Fig. 1). Relaxation by spin-rotation interaction depends neither on nuclear state, nor on spectral frequency, and therefore is included later.

The electron spin transition probabilities per unit time for nitrogen hyperfine manifold m_I are [17]:

$$W_e(m_I) \equiv W(M_S \rightarrow M_S \pm 1) = 2j^{eg}(\omega_e)B_0^2 + 4j^{gA}(\omega_e)B_0m_I + 2j^{AA}(\omega_e)m_I^2 \quad (1)$$

where j^{eg} and j^{AA} are modified spectral densities that arise respectively from the Zeeman and hyperfine (END) interactions alone, and $2j^{gA}$ is from the cross term. The angular electron resonance frequency is ω_e , and the static magnetic field strength is B_0 .

The nuclear spin transition probabilities per unit time for nitrogen spin I are [17]:

$$W_n(I) \equiv W(m_I \rightarrow m_I \pm 1) = \frac{1}{2}j^{AA}(\omega_a)[I(I+1) - m_I(m_I \pm 1)] \quad (2)$$

where $\omega_a = \frac{1}{2}a_0$ (in angular frequency units), and a_0 is the isotropic nitrogen hyperfine coupling. The nuclear transition probability is therefore: $W_n \equiv \frac{1}{2}j^{AA}(\omega_a)$ for a ^{15}N -nitroxide, and $W_n \equiv j^{AA}(\omega_a)$ for a ^{14}N -nitroxide.

The probabilities per unit time of combined electron and nuclear spin transitions, i.e., cross-relaxation, are [17]:

$$W_{x_1}(I) \equiv W(M_S, m_I \rightarrow M_S \pm 1, m_I \pm 1) = 2j^{AA}(\omega_e)[I(I+1) - m_I(m_I \pm 1)] \quad (3)$$

$$W_{x_2}(I) \equiv W(M_S, m_I \rightarrow M_S \pm 1, m_I \mp 1) = \frac{1}{3}j^{AA}(\omega_e)[I(I+1) - m_I(m_I \mp 1)] \quad (4)$$

where the isotropic dipolar spectral density is omitted [16]. The transition probabilities for cross-relaxation are therefore: $W_{x_1} = 2j^{AA}(\omega_e)$ and $W_{x_2} = \frac{1}{3}j^{AA}(\omega_e)$, for a ^{15}N -nitroxide; and are $W_{x_1} = 4j^{AA}(\omega_e)$ and $W_{x_2} = \frac{2}{3}j^{AA}(\omega_e)$, for a ^{14}N -nitroxide.

In the case of isotropic rotational diffusion, the modified spectral density for the electron-nuclear dipolar (END) interaction is given by [25,17]:

$$j^{AA}(\omega) = \frac{1}{30}((\Delta A)^2 + 3(\delta A)^2) \cdot \frac{\tau_R}{1 + \omega^2 \tau_R^2} = \frac{1}{20} \sum_{i=x,y,z} (A_{ii} - a_0)^2 \cdot \frac{\tau_R}{1 + \omega^2 \tau_R^2} \quad (5)$$

where τ_R is the rotational correlation time. The hyperfine anisotropies appearing in Eq. (5) are defined as $\Delta A = A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})$ and $\delta A = \frac{1}{2}(A_{xx} - A_{yy})$, and the isotropic coupling constant is $a_0 = \frac{1}{3}(A_{xx} + A_{yy} + A_{zz})$, with the hyperfine tensor (A_{xx}, A_{yy}, A_{zz}) expressed in angular frequency units. Analogous expressions apply for j^{eg} and j^{gA} , and those corresponding to anisotropic rotational diffusion are given in Ref. [16] (see also Ref. [26]).

From Eqs. (2), (3) and (5), we see that the cross-relaxation rate is related to the nuclear relaxation rate by: $W_{x_1} = 4W_n j^{AA}(\omega_e) / j^{AA}(\omega_a) = 4W_n(1 + \omega_a^2 \tau_R^2) / (1 + \omega_e^2 \tau_R^2)$. Only for very fast motion, when $\omega_e^2 \tau_R^2 < 1$, does cross-relaxation become comparable in rate to nuclear relaxation. However, cross relaxation rates are comparable to the pure END contribution to electron relaxation. From Eqs. (1) and (3), we find that $W_{x_1} = 4W_e(\text{END})$ for ^{15}N -nitroxides, and $W_{x_1} = 2W_e(\text{END})$ for the $m_I = \pm 1$ manifolds of ^{14}N -nitroxides. Therefore, we need to take cross relaxation into account when analyzing electron spin-lattice relaxation of spin labels.

3. Saturation recovery and SR-ELDOR for ^{15}N -nitroxides

In saturation recovery experiments, we pump with a single intense pulse of microwave radiation of frequency ω_p that saturates the EPR transition irradiated. We detect return to equilibrium by monitoring the transverse magnetisation with weak continuous radiation of frequency ω_{obs} [27]. The observer power is chosen to be sufficiently low as not to affect the degree of saturation. If we observe the same transition as that saturated ($\omega_{obs} = \omega_p$), we have

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