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Lifetimes of the singlet-states under coherent off-resonance irradiation in NMR spectroscopy

Karthik Gopalakrishnan [a], Geoffrey Bodenhausen [a,b,*]

[a] Laboratoire de Résonance Magnétique Biomoléculaire, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, BCH, CH-1015 Lausanne, Switzerland

[b] Département de Chimie, Associé au CNRS, Ecole Normale Supérieure, 24 rue Lhomond 75231, Paris Cedex 05, France

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Abstract

Singlet-states $|S\rangle = (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2}$ can be excited in pairs of coupled spins I and S, first by preparing either a non-vanishing zero-quantum coherence I^+S^- or a state of longitudinal two-spin order I_zS_z and then by applying a coherent radio-frequency (RF) irradiation with a carrier frequency $\omega_{rf} = (\Omega_I + \Omega_S)/2$ that lies half-way between the chemical shifts of the two spins involved. The life-times T_S can be much longer than the spin-lattice relaxation time T_1 of longitudinal magnetization, but singlet-states are ultimately relaxed, not only by dipolar interactions between the active spins or with the external spins, but also as a result of a non-vanishing offset $\Delta\omega = \omega_{rf} - (\Omega_I + \Omega_S)/2$ or an insufficient amplitude of the RF irradiation that fails to fulfill the condition $\omega_1 \gg \Delta\Omega = (\Omega_I - \Omega_S)$. In this work, the effect of off-resonance irradiation is explored and an approximate formula for the effective relaxation rate of the singlet population is provided on the basis of perturbation theory. The qualitative features of the dependence of the relaxation rate of the singlet population on the offset $\Delta\omega$ and on the difference $\Delta\Omega$ of the chemical shifts of the two spins are illustrated by comparison with numerical simulations.

Keywords: Singlet-state; Singlet-state lifetime; Zero-quantum coherence; Longitudinal two-spin order

1. Introduction

It has been shown by Levitt and co-workers [1–3] that singlet-states can be prepared in homonuclear two-spins systems so as to have lifetimes T_S that can be much longer than the longitudinal relaxation time T_1 of the spins involved. Many experiments that rely on the "memory" of the populations of eigen-states of spin systems, such as methods that have been designed to measure slow diffusion [4] or slow chemical exchange [5], were hitherto believed to be limited by the longitudinal relaxation time T_1. Such experiments can now be extended to much longer time-scales in as far as suitable singlet-states with $T_S > T_1$ can be excited. The lifetimes T_S of singlet-states can be very long provided their populations are isolated from other states, i.e., provided both coherent and stochastic Hamiltonians that give rise to relaxation are symmetric with respect to a permutation of the two spins. The dipolar interaction between the two spins involved necessarily possesses this symmetry and will therefore leave the population of the singlet-state unaffected. By contrast, the difference in the chemical shift anisotropies (CSAs) as well as dipolar couplings to external spins, do not possess this symmetry. There are always bound to be some leakage terms due to stochastically fluctuating Hamiltonians that are not under the control of the experimenter. Another source of leakage stems from the coherent parts of the Hamiltonian. These can, at least in principle, be controlled by applying suitable RF pulses. In the original experiments [2,4], a continuous-wave RF irradiation with the carrier positioned exactly half-way between the isotropic chemical shifts of the two spins I and S, i.e., at $\omega_{rf} = (\Omega_I + \Omega_S)/2$, allows one to effectively suppress the shifts, thereby making the effective

* Corresponding author. Fax: +41 21 6939435.
E-mail address: Geoffrey.Bodenhausen@epfl.ch (G. Bodenhausen).

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Hamiltonian symmetric with respect to permutation. As with many other average Hamiltonian strategies, the stronger the RF field (i.e., the better the inequality $\omega_1 \gg \Delta\Omega = (\Omega_I - \Omega_S)$ is fulfilled), the better is the suppression of the effects of the chemical shifts. The ratio $\Delta\Omega/\omega_1$ of the magnitude of the chemical shift difference and the RF amplitude is an important parameter that affects the singlet lifetime. The offset $\Delta\omega = \omega_{\text{rf}} - (\Omega_I + \Omega_S)/2$ of the carrier from the mean of the chemical shifts of the two spins is another source of leakage of the population of the singlet-state. The ratio $|\Delta\omega|/\omega_1$ of this offset and the RF amplitude is therefore another important parameter that determines the singlet lifetime. In the following, a simple theory is presented of the lifetime T_S of the population of a singlet-state in an isolated spin pair irradiated by a continuous RF field and relaxed only by the dipolar interaction between the two active spins. The Liouvillian of this system can be represented by a matrix of dimension 16×16. If one invokes a secular approximation with respect to the RF Hamiltonian, this matrix is block-diagonal. The population of the singlet-state is therefore only connected to a few other terms, thus allowing one to describe the dynamics by an effective Liouvillian of reduced dimensions which provides a qualitative understanding of the dependence of the lifetime of the singlet-state on the ratios $|\Delta\omega|/\omega_1$ and $\Delta\Omega/\omega_1$, i.e., on the offset $\Delta\omega$ and on the difference $\Delta\Omega$ of the isotropic shifts. Numerical simulations of relaxation in a two-spin system with a dipolar interaction between the active spins supplements the theory.

1.1. The Liouvillian

In the usual rotating frame, the Hamiltonian of a two-spin system irradiated by a continuous RF field is given by

$$\mathcal{H} = \omega_1(\mathcal{I}_x + \mathcal{S}_x) + \Delta\omega(\mathcal{I}_z + \mathcal{S}_z) + 2\pi J \mathcal{I}\cdot\mathcal{S} + \tfrac{1}{2}\Delta\Omega(\mathcal{I}_z - \mathcal{S}_z), \tag{1}$$

where ω_1 is the RF amplitude, $\Delta\omega = \omega_{\text{rf}} - (\Omega_I + \Omega_S)/2$ is the offset of the carrier ω_{rf} from the center of the spectrum $(\Omega_I + \Omega_S)/2$ and $\Delta\Omega = \Omega_I - \Omega_S$ is the difference of the isotropic shifts assumed to be positive without loss of generality. While the first three terms in Eq. (1) are invariant with respect to a permutation of the two spins, the last term is anti-symmetric. As we shall see, this leads to leakage of the population of the singlet-state to the triplet states. When $\Delta\omega/\omega_1 = 0$ and $\Delta\Omega/\omega_1 \ll 1$, the fourth term proportional to the shift-difference $\Delta\Omega$ is rendered ineffective since it does not commute with the leading RF term proportional to ω_1 that dominates the Hamiltonian. However, when the offset $|\Delta\omega|/\omega_1 > 0$, a part of the term proportional to $\Delta\Omega$ remains secular with respect to the dominant terms in Eq. (1). This may be appreciated by rewriting the Hamiltonian of Eq. (1) in a basis where the symmetric part of the Hamiltonian that is invariant to permutation appears diagonal.

$$\mathcal{H} = \omega_{\text{eff}}(\mathcal{I}_z + \mathcal{S}_z) + 2\pi J \mathcal{I}\cdot\mathcal{S} + \Delta\Omega[(\mathcal{I}_z - \mathcal{S}_z)\cos\beta - (\mathcal{I}_x - \mathcal{S}_x)\sin\beta], \tag{2}$$

where the effective frequency ω_{eff} and the angle β are given by

$$\omega_{\text{eff}} = \sqrt{(\omega_1)^2 + \Delta\omega^2}, \qquad \tan\beta = \omega_1/\Delta\omega. \tag{3}$$

If we treat the latter two anti-symmetric terms of the Hamiltonian in Eq. (2) as a perturbation, it is evident that the third term, which is proportional to $\cos\beta$, commutes with the leading symmetric term, and is therefore secular in the eigenbase of this symmetric term. The term $(\mathcal{I}_x - \mathcal{S}_x)\sin\beta$ is non-secular and will affect the dynamics very weakly provided $\Delta\Omega/\omega_{\text{eff}} \ll 1$. It will hence be neglected in what follows. In passing, we note that the singlet population retains its identity under the transformation from Eqs. (2) to (3). while all other observables are affected by this transformation. The Hamiltonian of Eq. (2) can be represented in the basis $|T_{+1}\rangle = |\alpha\alpha\rangle$, $|T_0\rangle = n(|\alpha\beta\rangle + |\beta\alpha\rangle)$, $|T_{-1}\rangle = |\beta\beta\rangle$, and $|S\rangle = n(|\alpha\beta\rangle - |\beta\alpha\rangle)$, where n is a normalization constant equal to $2^{-1/2}$.

$$\mathcal{H} = \omega_{\text{eff}}(|T_{+1}\rangle\langle T_{+1}| - |T_{-1}\rangle\langle T_{-1}|) + \pi J(|T_0\rangle\langle T_0| - |S\rangle\langle S|) + \Delta\Omega\cos\beta(|T_0\rangle\langle S| + |S\rangle\langle T_0|) - \pi J E_{T^0,S}, \tag{4}$$

where $E_{T^0,S}$ is the identity operator in the manifold spanned by $|T_0\rangle$ and $|S\rangle$, i.e., $E_{T^0,S} = |T_0\rangle\langle T_0| + |S\rangle\langle S|$. We observe that the Hamiltonian in Eq. (4) is the sum of two sub-Hamiltonians pertaining to the sub-spaces spanned by the operators $(|T_{+1}\rangle, |T_{-1}\rangle)$ and $(|T_0\rangle, |S\rangle)$. As far as the coherent part of the dynamics is concerned, the two sub-spaces are independent of each other. The sub-space of interest is the one containing the singlet population. The Hamiltonian in this sub-space can be written using four fictitious spin-half operators defined by,

$$\begin{aligned} E_{T^0,S} &= |T_0\rangle\langle T_0| + |S\rangle\langle S| \\ \mathcal{L}_z &= \frac{1}{2}(|T_0\rangle\langle T_0| - |S\rangle\langle S|) \\ \mathcal{L}_x &= \frac{1}{2}(|T_0\rangle\langle S| + |S\rangle\langle T_0|) \\ \mathcal{L}_y &= \frac{1}{2i}(|T_0\rangle\langle S| - |S\rangle\langle T_0|), \end{aligned} \tag{5}$$

as follows:

$$\mathcal{H}_{T,S} = 2\pi J \mathcal{L}_z + 2\Delta\Omega\cos\beta\mathcal{L}_x. \tag{6}$$

The evolution of the density operator under the Hamiltonian of Eq. (6) is governed by the following equation of motion for the three operators defined by Eq. (5).

$$\frac{d}{dt}\begin{pmatrix} \mathcal{L}_z \\ \mathcal{L}_y \\ \mathcal{L}_x \end{pmatrix} = \begin{pmatrix} 0 & 2\Delta\Omega\cos\beta & 0 \\ -2\Delta\Omega\cos\beta & 0 & -2\pi J \\ 0 & 2\pi J & 0 \end{pmatrix}\begin{pmatrix} \mathcal{L}_z \\ \mathcal{L}_y \\ \mathcal{L}_x \end{pmatrix}. \tag{7}$$

The operator $\mathcal{L}_z$ in Eq. (7) corresponds to the difference between the populations of the $|T_0\rangle$ component of the triplet manifold and the singlet-state. This is none other than the symmetric part of the zero-quantum coherence. Therefore, in so far as the coherent part of the dynamics is concerned, moving the carrier away from the center of the spectrum ($\Delta\omega \neq 0$) re-introduces the shift difference which is secular with respect to the leading dominant term of the Hamiltonian proportional to ω_{eff} in Eq. (2).

1.2. Relaxation

The relaxation rates can be calculated in the framework of Redfield theory [6,7]. The homonuclear dipolar interaction IS between the two spins I and S that are actively involved in the singlet-state is assumed to be the only source of relaxation in this analysis. The stochastic Hamiltonian that leads to relaxation can be written as a scalar product of the second rank spherical tensors corresponding to the spatial and spin parts as follows [7]:

$$\mathcal{H}_{IS}(t) = \omega_{\text{D}} \sum_q A_q(t) F_{-q}, \tag{8}$$

where $A_q(t)$ is the spatial part of the interaction that is randomly time-dependent due to molecular reorientation, F_{-q} are the components of the rank-2 spherical tensor formed by the product of the two spin operators and ω_{D} is the strength of the dipolar interaction. In calculating, the relaxation terms in the Liouvillian, an additional assumption is made in addition to the usual approximations of Redfield theory. If τ_{c} is the correlation time of the random process (usually due to rotational diffusion), and if ω_1 is the amplitude of the RF field, we shall assume that $\omega_1\tau_{\text{c}} \ll 1$. In other words, the random motion is assumed to obey the extreme narrowing condition with respect to the RF field amplitude ω_1, which is typically four to five orders of magnitude smaller than the Larmor frequency ω_0 that is used to define the usual extreme narrowing condition $\omega_0\tau_{\text{c}} \ll 1$. As a result of this assumption, the relaxation terms in the Liouvillian appear to be independent of the RF field amplitude ω_1, and are thus identical to the case where $\omega_1 = 0$ [8]. We may recall that essentially the same assumption is made in writing the Bloch equations in the presence of an RF field [8–11].

Owing to the scalar form of the stochastic Hamiltonian of Eq. (8), the Redfield relaxation matrix is block diagonal in the eigenbasis of the Zeeman super-Hamiltonian. The observables of the ($|S\rangle$, $|T_0\rangle^z$) manifold are therefore only connected to the populations of the $|T_{+1}\rangle^z$ and $|T_{-1}\rangle^z$ states. The superscripts z on the kets indicate that these terms are quantized along the z direction in contrast to the basis of Eq. (4), which corresponds to the tilted frame of reference introduced in Eq. (2), where the block diagonal nature of the Redfield matrix would be lost. We make a second approximation now by neglecting all terms in the relaxation matrix that are non-secular with respect to the effective field in Eq. (2). This approximation is valid as long as $\omega_{\text{eff}} \gg \omega_{\text{D}}^2\tau_{\text{c}}$ which is readiliy fulfilled in practice. When solving the Bloch equations in the presence of a continuous RF field, this is referred to as the “condition of saturation”. This approximation allows us to neglect all terms in the relaxation matrix that connect operators that nutate at different rates, resulting in a block diagonal form for the total Liouvillian matrix. The block containing the singlet population is

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} |S\rangle\langle S| \\ \mathcal{L}_y \\ \mathcal{L}_x \\ |T_0\rangle\langle T_0| \\ |T_{+1}\rangle\langle T_{+1}| \\ |T_{-1}\rangle\langle T_{-1}| \end{pmatrix} = \begin{pmatrix} 0 & -\Delta\Omega\cos\beta & 0 & 0 & 0 & 0 \\ \Delta\Omega\cos\beta & -R_2 & -2\pi J & -\Delta\Omega\cos\beta & 0 & 0 \\ 0 & 2\pi J & -R_2 & 0 & 0 & 0 \\ 0 & \Delta\Omega\cos\beta & 0 & -R_{0,0} & R_{0,+1} & R_{0,-1} \\ 0 & 0 & 0 & R_{0,+1} & R_{+1,+1} & R_{+1,-1} \\ 0 & 0 & 0 & R_{0,-1} & R_{+1,-1} & R_{-1,-1} \end{pmatrix} \times \begin{pmatrix} |S\rangle\langle S| \\ \mathcal{L}_y \\ \mathcal{L}_x \\ |T_0\rangle\langle T_0| \\ |T_{+1}\rangle\langle T_{+1}| \\ |T_{-1}\rangle\langle T_{-1}| \end{pmatrix}. \tag{9}$$

It is clear that the singlet-state is isolated from all other spin orders either if $\Delta\Omega = 0$ (where it would not be possible to excite any singlet-state) or if the RF carrier is positioned exactly half-way between the two chemical shifts ($\Delta\omega = 0$, hence $\cos\beta = 0$). It should however be borne in mind that for the present treatment to be valid, the RF needs to be strong enough to satisfy $\Delta\Omega/\omega_1 \ll 1$ since, the non-secular term $\Delta\Omega(\mathcal{I}_x - \mathcal{S}_x)\sin\beta$ in Eq. (3) could not be neglected otherwise. It should also be emphasized that despite the secular approximation involved in simplifying the Redfield relaxation matrix in the tilted frame, off-diagonal terms may occur in the relaxation matrix that connect the coherences $\mathcal{L}_x$ and $\mathcal{L}_y$ to the populations $\mathcal{L}_z$ in Eq. (9) since, all of these operators commute with the dominant part of the Hamiltonian, $\omega_{\text{eff}}(\mathcal{I}_z + \mathcal{S}_z)$ of Eq. (2). The symmetry of the dipolar interaction under a permutation of the two spins however ensures that off-diagonal terms connecting operators of different symmetry must vanish. The form of the Liouvillian matrix in Eq. (9) is hence rigorously correct. The frequencies and the relaxation rates can be obtained by diagonalization.

In the presence of an offset, the evolution of the singlet population must be described by an oscillating function with a multi-exponential envelope since it is no longer an eigenmode of the Liouvillian. An estimate of the lifetime T_S of the longest-lived eigenvector of the Liouvillian matrix of Eq. (9) can be obtained by examining the smallest eigenvalue. Treating $\Delta\Omega\cos\beta$ as a perturbation, the second-order correction to the relevant eigenvalue of the Liouvillian is

$$\Lambda^1 = -\frac{1}{4}\Delta\Omega^2\cos^2\beta\left(\frac{1}{R_2+2\pi iJ}+\frac{1}{R_2-2\pi iJ}\right). \quad (10)$$

This correction is purely real and results in a corrected relaxation rate of the singlet population given by,

$$R_S \approx \frac{1}{2}\Delta\Omega^2\cos^2\beta\left(\frac{R_2}{R_2^2+4\pi^2J^2}\right) = \frac{1}{2}\Delta\Omega^2\left(\frac{\Delta\omega^2}{\Delta\omega^2+\omega_1^2}\right)\left(\frac{R_2}{R_2^2+4\pi^2J^2}\right), \quad (11)$$

where the angle β has been defined in Eq. (3). Eq. (11) predicts that, for a given RF amplitude ω_1, the relaxation rate of the singlet-state population depends on the difference of the chemical shifts $\Delta\Omega = \Omega_I - \Omega_S$ in a quadratic fashion characteristic of second-order perturbation theory. When the RF carrier is positioned in the center of the spectrum ($\Delta\omega = 0$), the singlet population is completely isolated. On the other hand, when $|\Delta\omega|/\omega_1 \gg 1$, the rate R_S attains a limiting value,

$$R_S = \frac{1}{2}\Delta\Omega^2\left(\frac{R_2}{R_2^2+4\pi^2J^2}\right). \quad (12)$$

Eq. (11) can be re-written in terms of reduced quantities, $P = \Delta\Omega/(2\pi J)$ and $Q = \Delta\omega/\omega_1$

$$R_S \approx \frac{1}{2}P^2\left(\frac{Q^2}{1+Q^2}\right)\left(\frac{R_2}{1+\left(\frac{R_2}{2\pi J}\right)^2}\right). \quad (13)$$

2. Simulations

The evolution of the singlet-state population in the presence of a continuous RF field and dipolar relaxation were simulated numerically, assuming ($\omega_1\tau_c \ll 1$). Fig. 1 shows the evolution of the singlet population $P_S = \mathrm{Tr}(\sigma(t)|S\rangle\langle S|)$ as a function of the offset $\Delta\omega$, starting from an initial density operator comprising only a non-vanishing population of the singlet state, $|S\rangle\langle S|$. The parameters used in the simulations (given in the figure caption) are typical of systems of pairs of protons.

The population P_S of the singlet-state is seen to have shorter lifetimes with increasing offsets. The decay of the singlet-state on resonance for $\Delta\omega = 0$ (solid curve of Fig. 1) is due to the non-secular part of the Hamiltonian $\Delta\Omega(\mathcal{I}_x - \mathcal{S}_x)\sin\beta$ in Eq. (2) which was neglected in deriving Eq. (11). The dependence of the singlet relaxation rate on both the shift difference $\Delta\Omega$ and the offset $\Delta\omega$ is shown in Fig. 2. The singlet population P_S was calculated for pairs of values of these parameters at a time $t = 10$ s and the corresponding relaxation rate $R_S = 1/T_S$ was calculated

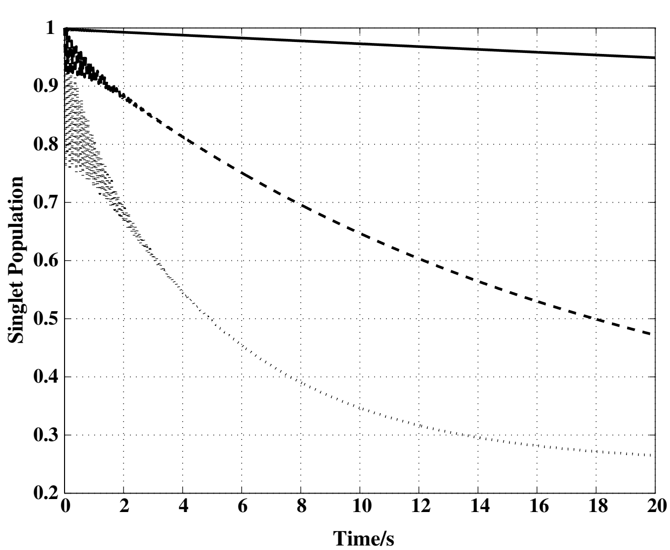

Fig. 1. Simulations of the time-dependence of the singlet population with $\Delta\Omega/2\pi = 75$ Hz, $\omega_1/2\pi = 1100$ Hz, $J/2\pi = 12$ Hz at $\Delta\omega/2\pi = 0$ Hz (solid line), 50 Hz (dashed curve), and 100 Hz (dotted curve). Relaxation was introduced with the parameters, $\omega_D/2\pi = 30$ kHz, $\tau_c = 0.1$ ns, and $\omega_0/2\pi = 400$ MHz.

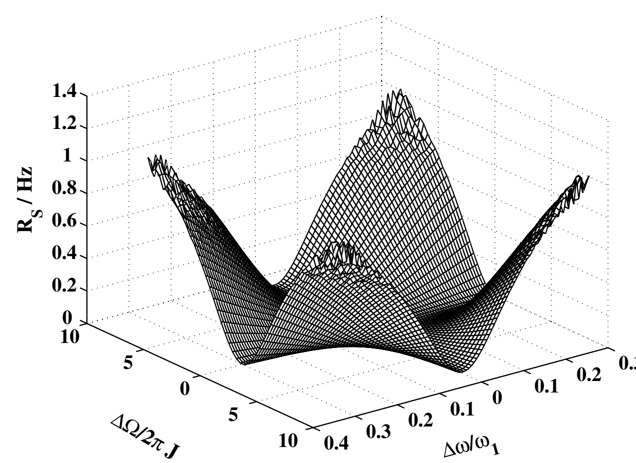

Fig. 2. Dependence of the singlet relaxation rate on the shift difference $\Delta\Omega$ and the offset $\Delta\omega$. The rest of the parameters are identical to those in Fig. 1.

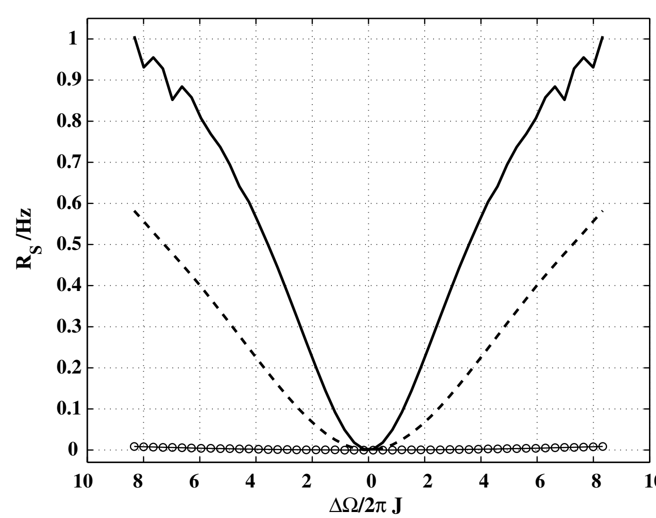

Fig. 3. Dependence of the singlet relaxation rate on the shift difference $\Delta\Omega$ at offsets $\Delta\omega = 0$ (zero) Hz (open circles), 150 Hz (dashed curve), and 300 Hz (solid curve).

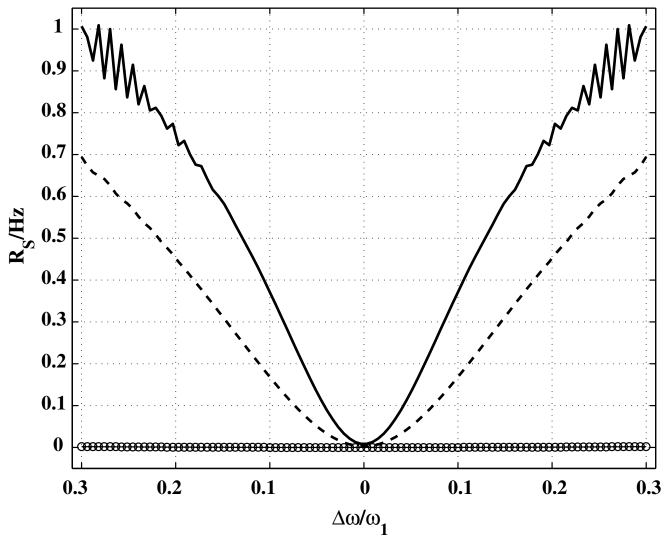

Fig. 4. Dependence of the singlet relaxation rate on the offset $\Delta\omega$ at shift differences $\Delta\Omega = 0$ Hz (open circles), 80 Hz (dashed curve), and 100 Hz (solid curve).

assuming a single exponential decay $\exp(-t/T_S)$. Fig. 3 shows the dependence of the relaxation rate $R_S = 1/T_S$ on the shift difference $\Delta\Omega$ for values of the offset $\Delta\omega = 0$, 150, and 300 Hz. The quadratic dependence on $\Delta\Omega$ is clearly seen with the width increasing with $\Delta\omega$. The curve with $\Delta\omega = 0$ corresponds to a relaxation rate that arises, again from the non-secular term which was neglected in Eq. (2).

In the same spirit, Fig. 4 shows the dependence of $R_S = 1/T_S$ on the offset $\Delta\omega$ for the values of the shift difference $\Delta\Omega = 0$, 80, and 100 Hz. The quadratic nature of the dependence is seen. When $\Delta\Omega = 0$, a change of offset does not affect the rate $R_S = 1/T_S$. This shows clearly that the shift difference $\Delta\Omega$ is the principal cause of relaxation of the singlet population P_S. In its absence, all other manipulations of the Hamiltonian will leave P_S undisturbed.

For given values of P and Q, Eq. (11) can predict the relaxation rate of the singlet state provided the rate R_2 is known. When R_2 is unknown, Eq. (11) can still be used to describe the singlet relaxation rate up to a multiplicative constant. The tolerance of the singlet relaxation rate to the parameters P and Q can however be predicted even without the knowledge of R_2. Fig. 5 illustrates this by comparing the normalized singlet relaxation rate predicted by Eq. (11) with simulations. The agreement is very satisfactory. Normalization was performed in both cases with respect to the fastest singlet relaxation rate. In all simulations, the dependence of R_S on P and Q is oscillatory for large values of P and Q. This is anticipated because the eigenvalues of the Liouvillian in Eq. (9) are complex.

3. Conclusions

The relaxation rates of populations of singlet-states in homonuclear spin pairs in the presence of continuous RF fields can be expressed by simple approximations. Although the present treatment does not include relaxation mechanisms other than the dipolar interaction between the actively involved spins, it can account for the dependence of the relaxation rate on the parameters $P = \Delta\Omega/(2\pi J)$ and $Q = \Delta\omega/\omega_1$ in a qualitative manner. These considerations are of prime importance for ongoing efforts to increase the lifetime of the singlet-state populations in view of studying slow dynamical processes.

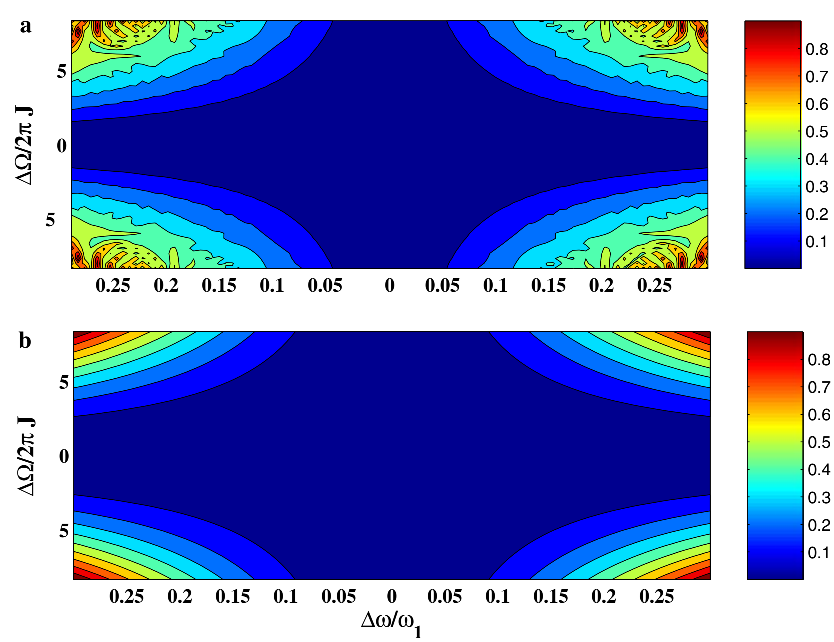

Fig. 5. The dependence of the singlet relaxation rate on the parameters P and Q, (a) simulation and (b) as predicted from Eq. (13).

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