

Interference between transverse cross-correlated relaxation and longitudinal relaxation affects apparent J -coupling and transverse cross-correlated relaxation

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Abstract

The apparent value of the measured J -coupling is affected by transverse cross-correlated relaxation between dipolar interaction and chemical shift anisotropy. This effect counteracts the decrease in the apparent value of J resulting from self-decoupling caused by longitudinal relaxation, thereby bringing the measured J -coupling closer to its true value. In addition to the dynamic frequency shift and self-decoupling, interference between transverse cross-correlated and longitudinal relaxation processes may serve as a complementary explanation for the deviation between the measured and true J -couplings for small size scalar couplings. The apparent cross-correlated relaxation rate between coupled spins may also be affected by this interference.

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1. Introduction

Accurate measurements of small J -couplings are important for deriving torsion angle restraints for protein-structure determination. These include the dependence of the $^3J(\text{H}_i^z, \text{H}_i^N)$ and $^3J(\text{H}_i^z, \text{N}_{i+1})$ couplings on the ϕ [1,2] and ψ [3] torsion angles, respectively. It has previously been reported that the apparent value of the measured J -coupling constant may deviate from its true value as a consequence of the difference in relaxation rate constants between in-phase and anti-phase coherence [4]. Dynamic frequency shift (DFS) [5], induced by cross-correlation between chemical shift anisotropy (CSA) and dipolar interactions, may also perturb the apparent J -coupling [6,7]. Without further discussion of the effect of DFS, we show in this communication that cross-correlated relaxation [8],

that is the difference in the relaxation rates between individual doublet components, may also alter the apparent J -coupling through interference with passive longitudinal relaxation, thereby counteracting the self-decoupling effect and bringing the measured J -coupling closer to its true value. The smaller the scalar coupling, the more significant this effect becomes.

2. Results and discussion

For a weakly scalar-coupled two-spin 1/2 system, IS , in which the scalar coupling is observed and measured on spin S , we consider two quantities: the transverse cross-correlated relaxation on spin S , δ_S [8], resulting from the interference between CSA and a dipolar interaction between the two spins; and the longitudinal relaxation on the passive spin I , R_{1I} . Using single-transition basis product operators (taking only positive coherence order into account), the time evolution of the coherence on spin S can be described in a two-dimensional Liouville subspace spanned by the basis operators S_+I^z and S_+I^{β} [9]:

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$$\frac{d}{dt} \begin{pmatrix} S_+ I^z \\ S_+ I^\beta \end{pmatrix} = \begin{pmatrix} i(\Omega_S + \lambda_S) - \rho + i(\pi J_{IS} + A_S) - \delta_S & R_{1I}/2 \\ R_{1I}/2 & i(\Omega_S + \lambda_S) - \rho - i(\pi J_{IS} + A_S) + \delta_S \end{pmatrix} \begin{pmatrix} S_+ I^z \\ S_+ I^\beta \end{pmatrix} \quad (1)$$

where $S_+ = S_x + iS_y$; J_{IS} is the scalar coupling constant (in units of Hz); δ_S is the transverse relaxation rate of spin S due to cross-correlation between its CSA and its dipolar interaction with spin I ; the longitudinal relaxation rate R_{1I} is dominated by dipolar coupling to neighboring spins; ρ is the average of the transverse relaxation of spin S in-phase and anti-phase relative to spin I ; Ω_S is the chemical shift of spin S ; and λ_S and A_S are the dynamic frequency shifts due to dipole and CSA auto-correlation and dipole–CSA cross-correlation, respectively. From Eq. (1) it can be seen that λ_S will induce a change in the apparent chemical shift while A_S will change the apparent J -coupling [4,5]. These two terms are not discussed in further detail in this Letter. By setting $\Omega_S + \lambda_S = 0$ and diagonalizing the matrix, the apparent J -coupling (without consideration of sign), J_{app} , and the apparent cross-correlated relaxation rate, δ_{app} , are given by the imaginary and the real parts, respectively, of the difference between the two eigenvalues. Thus, we obtain:

$$J_{app} = \sqrt{\frac{\sqrt{(R_1^2 + \delta^2 - J_{IS}^2)^2 + 4\delta^2 J_{IS}^2} - (R_1^2 + \delta^2 - J_{IS}^2)}{2}} \quad (2)$$

$$\delta_{app} = \pi \sqrt{\frac{\sqrt{(R_1^2 + \delta^2 - J_{IS}^2)^2 + 4\delta^2 J_{IS}^2} + (R_1^2 + \delta^2 - J_{IS}^2)}{2}} \quad (3)$$

where $R_1 = R_{1I}/2\pi$, and $\delta = \delta_S/\pi$.

In the limit of $\delta_S = 0$, Eq. (2) shows that the apparent J -coupling is only affected by self-decoupling as described by Harbison [3]. Thus, for $J_{IS} > R_1$, $J_{app} = (J_{IS}^2 - R_1^2)^{1/2}$; for $R_1 \geq J_{IS}$, $J_{app} = 0$. Note, when $R_1 \gg J_{IS}$, J_{app} is zero owing to the high spin flip rate; however, even for R_1 equal to or moderately larger than J_{IS} , the two coupled components $S_+ I^z$ and $S_+ I^\beta$ collapse to a single broad peak.

The dependence of the apparent J -coupling, J_{app} , and apparent cross-correlated relaxation rate, δ_{app} , on the longitudinal relaxation rate of spin I , R_{1I} , and the transverse cross-correlated relaxation rate of spin S , δ_S , is depicted in the form of three-dimensional plots in Fig. 1. The impact of δ_S on J_{app} is illustrated in Fig. 2A which shows the

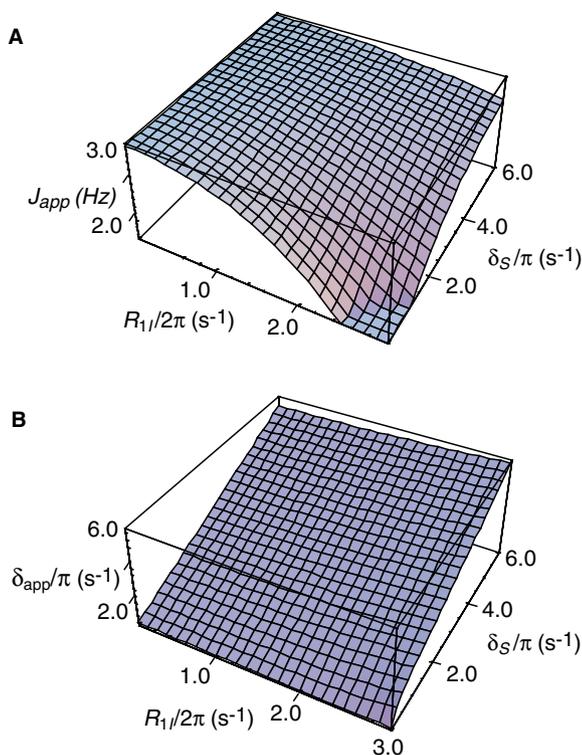


Fig. 1. Dependence of: (A) the apparent J -coupling, J_{app} , and (B) the apparent cross-correlated relaxation rate, δ_{app} , on the longitudinal relaxation rate of spin I (R_{1I}) and the transverse cross-correlated relaxation rate of spin S (δ_S) for a J_{IS} value of 3 Hz.

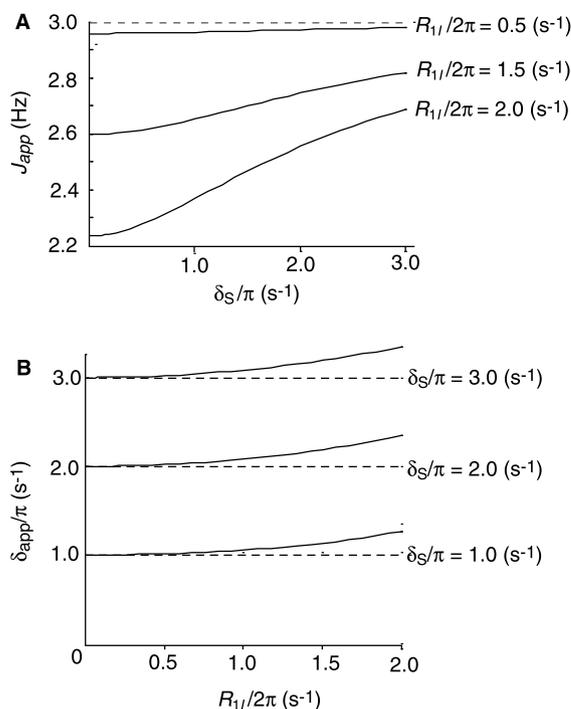


Fig. 2. Dependence of: (A) the apparent measured J -coupling (J_{app}) on the transverse cross-correlated relaxation of spin S (δ_S) for values of $R_{1I}/2\pi = 0.5, 1.5$ and $2.0 s^{-1}$, and (B) the apparent cross-correlated relaxation rate (δ_{app}) on the longitudinal relaxation of spin I (R_{1I}) for values of $\delta_S/\pi = 1.0, 2.0$ and $3.0 s^{-1}$. The curves are calculated for a value of $J_{IS} = 3$ Hz.

dependence of J_{app} on δ_S for different values of R_{1I} . The effect of interference between R_{1I} and δ_S on δ_{app} is shown in Fig. 2B where δ_{app} is plotted as a function of R_{1I} for different values of δ_S . From these plots, it is clear that the presence of non-zero transverse correlated relaxation for spin S results in an increase in the apparent value of J_{IS} , thereby compensating for the opposing effect resulting from self-decoupling.

The effects depicted in Figs. 1 and 2 are relevant for the parameter values typically found for an $\text{H}^{\text{N}}(S)\text{--H}^{\alpha}(I)$ spin system in an α -helix: assuming that ${}^3J(\text{H}^{\text{N}}\text{--H}^{\alpha}) = 3$ Hz; R_1^z is dominated by dipole/dipole interaction between H_i^z and its neighboring protons (e.g. H_i^{N} , $\text{H}_{i+1}^{\text{N}}$); $\Delta_{\text{CSA}}(\text{H}^{\text{N}}) = -8$ ppm and the angle between the principal axis of the H^{N} CSA tensor and the $\text{H}^{\text{N}}\text{--H}^{\alpha}$ bond vector is 20° [10]; the following values of $\delta(\text{H}^{\text{N}})$ and R_1^z are calculated at a polarizing field of 900 MHz (for ${}^1\text{H}$): ~ 7 s $^{-1}$ and ~ 7 s $^{-1}$, respectively, for $\tau_c = 10$ ns; ~ 13 s $^{-1}$ and ~ 12 s $^{-1}$, respectively, for $\tau_c = 20$ ns; ~ 19 s $^{-1}$ and ~ 16 s $^{-1}$, respectively, for $\tau_c = 30$ ns. As shown in Fig. 2A, for a protein with a rotational correlation time τ_c of 20 ns (corresponding to a molecular weight of about 40 kDa) the change in the value of the apparent cross-correlated relaxation rate, δ_{app} , resulting from interference between transverse cross-correlated and longitudinal relaxation processes could be up to approximately 1.5 s $^{-1}$, with a concomitant increase in the apparent J -coupling of ca. 0.5 Hz.

Finally, it is worth noting that if dynamic frequency shift (DFS) induced by cross-correlation between chemical shift anisotropy (CSA) and dipolar interactions is taken

into account, the term J_{IS} in Eqs. (2) and (3) is replaced by $J_{IS} + A_S/\pi$. In this case, the apparent J -coupling will be affected by three factors and their mutual interference: (1) the transverse relaxation of spin S due to the cross-correlation between its CSA and its dipolar interaction with spin $I(\delta_S)$, (2) the longitudinal relaxation of spin $I(R_{1I})$, and (3) the dynamic frequency shifts due to dipole–CSA cross-correlation (A_S).

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