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Relaxation of Longitudinal Three-Spin Order

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Nuclear magnetic resonance relaxation studies are an important tool for the study of molecular dynamics in liquids. Recent advances in both NMR theory and experimental techniques have substantially increased the level of information of molecular dynamics in liquids. The development of multiple-quantum relaxation (MQR) (*1*) has paved new ways to study the molecular dynamics in liquids. The advent of the MQR experiment opens the possibility of selecting the appropriate spin interaction which generates only a certain order of MQR. Multiple-quantum relaxation via transverse relaxation for degenerate spin systems has been applied to the study of slow molecular motion in macromolecules and molecular aggregates (*2, 3*). For longitudinal relaxation, several authors have demonstrated that dipole–dipole cross-relaxation may lead to the conversion of Zeeman order into three-spin order (*4*). Particularly in the work of Böhlen *et al.*, a so-called "pseudo-two-dimensional" spectrum has been obtained to demonstrate the effect of dipole–dipole cross-relaxation (*4*). In the present work, we report the result of a study which utilizes the one-dimensional analog of the triple-quantum 2D experiment via longitudinal relaxation to determine the relaxation behavior of three-spin order for the methyl protons in the deoxycholate (DOC) micelle system.

The pulse sequence used for measuring the relaxation of three-spin order is basically a multiple-quantum-filter pulse sequence as depicted in Fig. 1. The phases of the receiver and of the various pulses in the phase-cycling scheme were reported earlier (*3, 5–7*) for a triple-quantum filter. In order to eliminate the transverse contribu-

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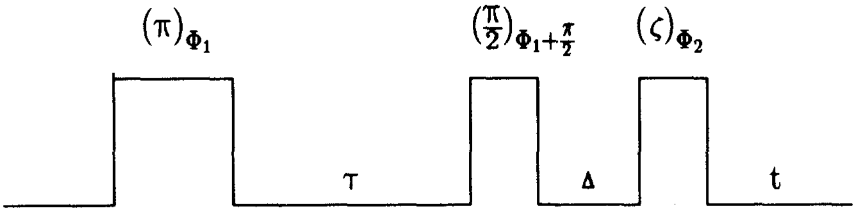

FIG. 1. The pulse sequence for the triple-quantum-filter experiment. ϕ_1 and ϕ_2 are set according to the phase-cycling scheme as described in Refs. (*3*, *5–7*).

tion of triple-quantum coherence due to the imperfection of the π pulse, 180° phase alternations in the inversion pulse are added in the phase-cycling scheme.

The description of the relaxation processes may be given in terms of the evolution of the density matrix in accordance with these pulse sequences. Since there is no two-spin order for an A_3 spin system we will limit our treatment to the proton relaxation of three-spin order in the methyl group. The spin–lattice interaction Hamiltonian of this system is defined by

$$\mathscr{H}(t) = \sum_{i<j} \epsilon_{ij} \sum_m (-1)^m T_2^m(i,j) Y_2^{-m}(\phi_{ij}) + \sum_i \gamma_i \sum_m (-1)^m T_1^m(i) B_1^{-m}(i,t), \quad [1]$$

where we follow the notations defined in Ref. (*2*) such that $\epsilon_{ij} \equiv (\sqrt{6\pi}/5)\gamma_i\gamma_j\hbar/r_{ij}^3$, $T_s^m(i,j)$ is a spin tensor operator of rank s, $Y_2^{-m}(\phi_{ij})$ is a spherical harmonic function of rank 2, $B_1^{-m}(i,t)$ is a lattice random field interaction operator, γ_i is the gyromagnetic ratio of species i of the methyl protons, and r_{ij} is the distance between protons i and j in the methyl group. The first term is due to the intramolecular dipolar interactions with $s = 2$ among the three protons of the methyl group and the second term is due to other unspecified interactions which are approximated by the isotropic random field model with $s = 1$; i.e., $|B_1^0(i,t)|^2 = |B_1^1(i,t)|^2 = |B_1^{-1}(i,t)|^2$.

In the periods in which the three-spin order evolves, and in the final detection period, the Redfield theory (*8*) is utilized to account for the relaxation processes for the methyl protons. The evolution of the density matrix ρ follows the equation of motion

$$\frac{d\rho}{dt} = \mathbf{R}\rho, \quad [2]$$

where $\mathbf{R}$ is the Redfield relaxation matrix which may be constructed for longitudinal relaxation in accordance with the interaction Hamiltonian defined in Eq. [1]. The density matrix ρ is defined as

$$\tilde{\rho} = [\rho_{11}, \rho_{44}, \rho_{77}, \rho_{88}, \rho_{22}, \rho_{66}, \rho_{33}, \rho_{55}]. \quad [3]$$

The matrix elements are labeled according to the spin energy levels as shown in Fig. 2.

To describe the interferences between the various modes of motion, which include internal rotation and wobbling motion of the methyl group and the overall reorientation of the micellar aggregate or the macromolecule, the cone model of Brainard and Szabo (*9*) is used to facilitate the calculation of the auto- and cross-correlation spec-

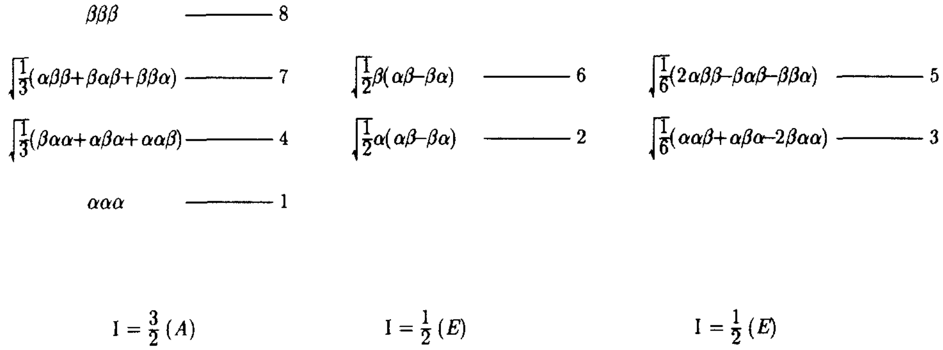

FIG. 2. Energy level diagram and basis functions for the A_3 spin system. The symmetry of the basis functions is indicated in parentheses.

tral densities. In this model, the dynamics of the molecular aggregates or the macromolecules are described by an isotropic slow reorientation of the whole molecule (or aggregate) and the fast internal motions for the methyl groups of interest. With the consideration of the auto- and cross-correlation of dipolar relaxations (*10*) among the three protons, the auto- and cross-spectral density functions used in the calculation of the relaxation matrix elements are given by

$$\begin{aligned}J^{mn}_{ijkl}(\omega) &\equiv \epsilon_{ij}\epsilon_{kl}(-1)^n \int_0^\infty \langle Y_2^m(\phi_{ij}(t))Y_2^{-n}(\phi_{kl}(t+\tau))\rangle \cos\omega\tau d\tau \\ &= \delta_{m-n}\frac{3\gamma^4\hbar^2}{10r^6}\left\{\frac{1}{4}S^2\frac{6D}{(6D)^2+\omega^2}+\frac{1}{4}\frac{(1-S^2)[6D+6D_w/(1-S^2)]}{[6D+6D_w/(1-S^2)]^2+\omega^2}\right. \\ &\quad +\frac{3}{4}\cos(\Omega_{ijkl})\frac{S^2(6D+4D_i)}{[(6D+4D_i)^2+\omega^2]} \\ &\quad \left. +\frac{3}{4}\cos(\Omega_{ijkl})\frac{(1-S^2)[6D+4D_i+2D_w/(1-S^2)]}{[6D+4D_i+2D_w/(1-S^2)]^2+\omega^2}\right\}, \qquad [4]\end{aligned}$$

where $\cos(\Omega_{ijkl}) = 1$ for $r_{ij} = r_{kl}$ and $\cos(\Omega_{ijkl}) = -\frac{1}{2}$ for $r_{ij} \neq r_{kl}$ to account for the auto- and cross-relaxations, respectively. It is assumed that the overall reorientational motion of the micelle has a correlation time $\tau_o = 1/6D$, the internal rotation of the methyl group has a correlation time $\tau_i = 1/4D_i$, and the wobbling motion of the methyl C_3 axis has a correlation time $\tau_w = 1/6D_w$. The wobbling motion is assumed to be within a cone of θ with a constant distribution and an order parameter S which is defined by (*9*)

$$S = \cos\theta(1+\cos\theta)/2. \qquad [5]$$

For the treatment of isotropic random field interaction, the corresponding spectral density function is defined by

$$j(n\omega) = (-1)\gamma_H^2\delta_{ij}\int_0^\infty \langle B_I^{+n}(i,0)B_I^{-n}(j,t)\rangle \cos(n\omega t)dt. \qquad [6]$$

After the first $\pi/2$ pulse, the triple-quantum coherence becomes

$$\begin{aligned}\rho_{18}(\tau^+) &= \rho^*_{81}(\tau^+)\\ &= (\rho_{11}(\tau^-) - 3\rho_{44}(\tau^-) + 3\rho_{77}(\tau^-) - \rho_{88}(\tau^-)).\end{aligned} \qquad [7]$$

Here we use the plus (or minus) sign in the superscript to represent the density matrix just after (or before) the pulse. The expression in the right hand side of Eq. [7] may be rewritten into operator formalism as $[5I^j_zI^k_zI^l_z - I^j_z(\mathbf{I}^k\cdot\mathbf{I}^l) - I^k_z(\mathbf{I}^l\cdot\mathbf{I}^j) - I^l_z(\mathbf{I}^j\cdot\mathbf{I}^k)]$, where $I^j_zI^k_zI^l_z$ is defined as the three-spin order operator for spins j, k, and l (*11*). Equation [7] shows that the nonuniform relaxations of the longitudinal elements ρ_{11} (or ρ_{88}) and ρ_{44} (or ρ_{77}) give rise to the creation of multiple-quantum coherence.

The evolution time Δ of the multiple-quantum coherence should be set much shorter than the transverse relaxation time so that relaxation may be neglected during this interval. In the present work, a Δ of 20 μs was used. After the application of the monitor pulse, the signals of various order of multiple-quantum coherences are converted into single-quantum coherence for observation. The selective observation of a certain order of multiple-quantum coherence can be achieved by the appropriate phase-cycling schemes reported (*3, 5–7*) previously. The elements of the density matrix $\rho(t)$ for observation of triple-quantum coherence become

$$\begin{aligned}\rho_{14}(\tau+\Delta^+) &= \frac{-\sqrt{3}}{8}(\cos 3\zeta - \cos\zeta)\rho_{18}(\tau+\Delta^-)\\ \rho_{47}(\tau+\Delta^+) &= \frac{3}{8}(\cos 3\zeta - \cos\zeta)\rho_{18}(\tau+\Delta^-)\\ \rho_{78}(\tau+\Delta^+) &= \frac{-\sqrt{3}}{8}(\cos 3\zeta - \cos\zeta)\rho_{18}(\tau+\Delta^-).\end{aligned} \qquad [8]$$

The pulse angle of the monitoring pulse ζ is set to the magic angle (54.74°) in order to optimize the signal. If $\zeta = \pi/2$ is used, no signal due to triple-quantum coherence can be observed.

The magnetization $\mathbf{M}_x$ observed during the detection period $t > \tau + \Delta$ is then evaluated by

$$\mathbf{M}_x = \gamma\hbar\ \mathrm{Tr}(\rho\mathbf{I}_x) \propto (\sqrt{3}\rho_{14} + 2\rho_{47} + \sqrt{3}\rho_{78} + \sqrt{3}\rho^*_{14} + 2\rho^*_{47} + \sqrt{3}\rho^*_{78}). \qquad [9]$$

During the acquisition period, nonuniform relaxation of the transverse elements ρ_{14}, ρ_{47}, and ρ_{78} gives rise to the creation of the finite spectral density arising from the cross-relaxation.

The measurements of triple-quantum coherence have been obtained for the methyl groups of DOC in a 75 m*M* D_2O micellar solution at 301 K with a Bruker AM-300 spectrometer operating at 7.05 T. Since the signal of methyl 18 is better resolved than those of the methyl 19 and 21 groups, we will focus our attention on the results for this methyl group. The experimental intensity profile of the methyl proton relaxation of three-spin order is shown in Fig. 3.

In a previous study, we determined a set of parameters, as listed in Table 1, which were obtained not only by fitting the proton MQR T_1 and T_2 but also by fitting multi-

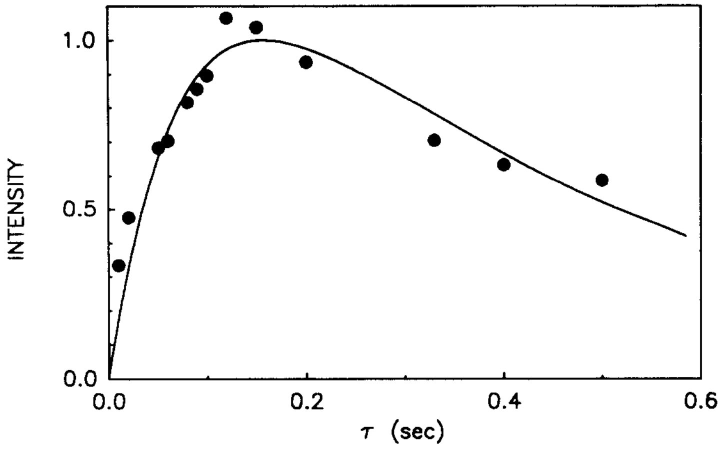

FIG. 3. Proton triple-quantum peak intensity as a function of evolution time for methyl 18 of the 75 m*M* DOC micelle in a 0.1 *M* Na_2CO_3, pD 9.0, aqueous solution at 301 K.

field carbon-13 T_1, NOE, and differential line-broadening effects in the proton-coupled ^{13}C spectrum. The theoretical curve is also shown in Fig. 3 for comparison. In the intensity profile for longitudinal relaxation, the calculated maximum intensity appears around 150 ms, while for transverse triple-quantum relaxation it was found around 35 ms (*3*). As it was pointed out previously (*2, 3*) for transverse double- and triple-quantum relaxation, the nonuniform relaxation of the transverse elements due to dipolar cross-relaxation in the quartet levels results in the creation of multiple-quantum coherence. However, in the presence of dipole–dipole cross-interaction, the dipolar coupling between quartet levels and doublet levels plays the key roles in the creation of nonuniform relaxations of longitudinal elements. Since the micellar system satisfies the motional conditions $\omega_H\tau_o > 1$, $\omega_H\tau_i \ll 1$, and $\omega_H\tau_w \ll 1$, where ω_H is the Larmor frequency of the NMR experiment, the relaxation profile of three-spin order is found to be rather insensitive to the variation of τ_o. Increasing magnitude of τ_i or τ_w results in a shift of maximum intensity to a shorter time and an early decay profile. Similar trends were also observed with the increase of $|j(\omega)|$ and, more important, the magnitude of these three-spin order signals in general increases with the value of order parameter. Without the dipole–dipole cross terms the calculated signal

TABLE I

Dynamic and Order Parameters Utilized in the Calculation of Three-Spin Order Relaxation in Accordance with the Cone Model

S	τ_o (ns)	τ_i (ps)	τ_w (ps)	$j(0)^a$	$j(\omega)$
0.64	4.5	7.6	22.1	15.5	−1.00

[a] Evolution of longitudinal three-spin order is not affected by the $j(0)$ term.

intensity of three-spin order vanishes. Thus the variation of the peak intensity in the relaxation processes of three-spin order demonstrates the importance of cross-correlation among the methyl protons. The relaxation of longitudinal three-spin order may then be utilized as a complementary method in the study of molecular dynamics in liquids.

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REFERENCES

1. A. WOKAUN AND R. R. ERNST, *Mol. Phys.* **36,** 317 (1978).
2. L. E. KAY AND J. H. PRESTEGARD, *J. Am. Chem. Soc.* **109,** 3829 (1987).
3. T. C. WONG, P. L. WANG, D. M. DUH, AND L. P. HWANG, *J. Phys. Chem.* **93,** 1295 (1989).
4. M. BÖHLEN, S. WIMPERIS, AND G. BODENHAUSEN, *J. Magn. Reson.* **77,** 589 (1988).
5. A. WOKAUN AND R. R. ERNST, *Chem. Phys. Lett.* **52,** 407 (1977).
6. U. PIANTINI, O. W. SØRENSEN, AND R. R. ERNST, *J. Am. Chem. Soc.* **104,** 6800 (1982).
7. L. BRAUNSCHWEILER, G. BODENHAUSEN, AND R. R. ERNST, *Mol. Phys.* **48,** 533 (1983).
8. A. G. REDFIELD, *in* "Advances in Magnetic Resonance" (J. S. Waugh, Ed.), Vol. 1, p. 1, Academic Press, New York, 1965.
9. J. R. BRAINARD AND A. SZABO, *Biochemistry* **20,** 4618 (1981).
10. J. R. HUBBARD, *J. Chem. Phys.* **52,** 563 (1970).
11. L. G. WERBELOW AND D. M. GRANT, *in* "Advances in Magnetic Resonance" (J. S. Waugh, Ed.), Vol. 9, p. 189, Academic Press, New York, 1977.