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RELAXATIONS STUDIES OF $2I_zS_z$ SPIN ORDER WITH SIGNAL ENHANCEMENT BY COHERENCE TRANSFER

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The pulse sequence for generating coherence transfer (or polarization transfer) is invoked to enhance the signal of heteronuclear two spin order (e.g. $2I_ZS_Z$) in a spin system with CH moiety. This allows the observation of selective conversion of Zeeman order, in a sample with natural abundant ^{13}C nuclei, into two spin order for measuring cross-correlation of chemical shift anisotropy and dipole-dipole interactions. The molecular reorientational correlation time and the orientation of the C–H axis with respect to the principal axes of carboxyl CSA tensor may be determined simultaneously in the relaxation profile of two spin order.

INTRODUCTION

Nuclear magnetic resonance relaxation studies are an important tool for the study of molecular dynamics in liquids. Recent advances in both the NMR theory and the experimental techniques have substantially increased its level of information. The development of multiple quantum relaxation (MQR)[1] has paved new ways to study the molecular dynamics in liquids. The advent of MQR experiment has opened the possibility to select 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].

Recently, the development of the theory of differential line broadening (DLB) has been applied to the cross relaxation between the chemical shift anisotropy (CSA) and the dipole-dipole (DD) interactions[4,5]. However, both the DLB effect and the generation of the "forbidden" multiple quantum coherence is dependent on the slow motional correlation time of the system. For those effects to be experimentally observable, this requirement has placed a rather strict limitation on the sytem suitable for such study.

In the case of longitudinal relaxation, several authors have demonstrated that the dipole-dipole cross relaxation may lead to the conversion of Zeeman order into three spin order in homonuclear three-spin system[6,7]. For molecules with CH spin system in fast motional region, the selective conversion of Zeeman order into heteronuclear two spin order (e.g. $2I_zS_z$) has been observed by Jaccard et al. for measuring cross-correlation of CSA and DD interactions[8]. The result is interpreted in terms of the orientation of ^{13}C–^{1}H internuclear vector with respect to the principal axes of the ^{13}C CSA tensor. However, the use of enriched carbon-13 sample in their work requires specific labelling which is too laborious in most cases. Therefore, techniques which utilize the naturally abundant nuclei to study the DD-CSA cross relaxations should be very attractive.

In the present work, we will report the result of a study which has taken advantage of the pulse

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Dedicated to Professor K. T. Wang on the occasion of his 60th birthday.

sequence for generating coherence transfer[9] to enhance the signal of two-spin order and to determine simultaneously the reorientational correlation time and the orientation of the C–H axis with respect to the principal axes of CSA tensor in a solution of methyl formate with natural abundant ^{13}C nuclei.

THEORY

The pulse sequence used for measuring the relaxation of the $2I_zS_z$ spin order basically invokes coherence transfer sequence as the initial preparation of the spin system:

$$(\pi/2)^{H}_{x}-1/(2J_{C-H})-(\pi/2)^{H}_{\phi}-t-(\pi/2)^{C}_{y}-(FID)$$

where the spin-spin coupling constant J_{C-H} is expressed in Hz. The first two proton 90° pulses are used for generating $^1H \rightarrow {}^{13}C$ coherence-transfer and the last 90° pulse of ^{13}C that follows converts it into the signal of two spin order for observation. Since the period, $1/(2J_{C-H})$, for generating coherence transfer is much shorter than T_1 of the system, it should be noted that spin relaxation during this period is neglected. Thus, the initial density matrix just after the preparation of the spin system with coherence transfer[9] is given by

$$\rho(t=0)\cong(1/4)(1+\hbar\omega_S S_z/kT\pm\hbar\omega_I(2S_zI_z)/kT) \quad (1)$$

where ω_S and ω_I are the Larmor frequencis of ^{13}C (denoted as S spin) and ^1H (denoted as I spin) nuclei, respectively. The +/− sign in the third term of Eq. (1) is taken according to the phase of the second 90° pulse of proton ($\phi = \pm y$). Difference spectra of ^{13}C with $\phi = \pm y$ are recorded for each value of the evolution time t in the pulse sequence. An anti-phase doublet spectral lines are observed. As expressed in Eq. (1), the difference in the intensity of the two (anti-phase) lines is related to the evolution of $2S_zI_z$ terms with signal enhancement by a factor of $\omega_I/\omega_S=\gamma_H/\gamma_C\cong 4$ as compared with the normal ^{13}C spectra[8].

The description of the relaxation processes during time t in which the $2I_zS_z$ coherence evolves may be described by the Redfield theory[10] which considers the CSA interaction at ^{13}C and ^1H. To account for the NMR relaxation processes, the populations of an IS system with two nonequivalent spin-1/2 nuclei may be described by the density matrix operator or in terms of the expectation values of the three operators I_z, S_z and $2I_zS_z$[11]. A straightforward calculation based on Redfield's scheme yields the coupling coefficients that determine the time evolution of these expectation values. The equation of motion has been given explicitly by Jaccard *et al.*[8] and their definitions of notations are followed,

$$\frac{d}{dt}\begin{bmatrix} <\Delta I_z(t)> \\ <\Delta S_z(t)> \\ <2I_zS_z(t)> \end{bmatrix} = \begin{bmatrix} A & D & 0 \\ D & B & E \\ 0 & E & C \end{bmatrix}\begin{bmatrix} <\Delta I_z(t)> \\ <\Delta S_z(t)> \\ <2I_zS_z(t)> \end{bmatrix} \quad (2)$$

where $<\Delta I_z(t)>\equiv<I_z(t)>-<I_z(\infty)>$, $<\Delta S_z(t)<\equiv< S_z(t)>-<S_z(\infty)>$. The expectation values at infinite time denote their thermal equilibrium averages. The coupling coefficients are defined by

$$A\equiv-(10/3)J_{IS,IS}$$

$$B\equiv-(10/3)J_{IS,IS}-4J_{S,S}$$

$$C\equiv-2J_{IS,IS}-4J_{S,S}$$

$$D\equiv-(5/3)J_{IS,IS}$$

$$E\equiv-4J_{IS,S} \quad (3)$$

where $J_{IS,IS}$, $J_{S,S}$ and $J_{IS,S}$ represent the spectral density functions for the DD, CSA and DD-CSA cross relaxations, respectively. For simplicity, only isotropic motion with extreme narrowing condition is considered, e.g., $\omega\tau_c<<1$ where τ_c is the reorientational correlation time of the molecules considered. Other relaxation mechanisms such as remote intramolecular and intermolecular DD interactions are neglected. The spectral density functions can thus be simplifed into the following expressions:

$$J_{IS,IS} \equiv (3/10)\gamma_I^2 \gamma_S{}^2 \hbar^2 r^{-6} \tau_c$$
$$J_{S,S} \equiv (1/30)(\gamma_S B_0)^2 L(\sigma)\tau_c$$
$$J_{IS,S} \equiv -(1/20)\gamma_I \gamma_S{}^2 \hbar r^{-3} B_0 K(\sigma, \theta_{xz'}, \theta_{yz'})\tau_c \tag{4}$$

where r is the proton-carbon internuclear distance. Also, we define

$$L(\sigma) \equiv \sigma_x{}^2 + \sigma_y{}^2 + \sigma_z{}^2 - \sigma_x\sigma_y - \sigma_y\sigma_z - \sigma_z\sigma_x \tag{5a}$$

and

$$K(\sigma, \theta_{xz'}, \theta_{yz'}) \equiv (\sigma_x - \sigma_z)(3\cos^2\theta_{xz'} - 1) + (\sigma_y - \sigma_z)(3\cos^2\theta_{yz'} - 1) \tag{5b}$$

where σ_x, σ_y and σ_z are the principal components of shielding tensor. The angles $\theta_{xz'}$ and $\theta_{yz'}$ define the relative orientation between the IS internuclear vector ($^1H-{}^{13}C$) with respect to the principal axes x and y of σ tensor, respectively.

The time-evolution of $\langle\Delta S_z(t)\rangle$ may be solved from Eq. (2) with the known values of $\langle\Delta I_z(0)\rangle$, $\langle\Delta S_z(0)\rangle$ and $\langle 2I_zS_z(0)\rangle$ which may be calculated with the help of the initial density matrix given in Eq. (1) and the final equilibrium distribution. We obtained $\langle\Delta I_z(0)\rangle = -\hbar\omega_I/(4KT)$, $\langle\Delta S_z(0)\rangle = 0$ and $\langle 2I_zS_z(0)\rangle = \pm\hbar\omega_I/(4kT)$.

The difference in the intensity, denoted by ΔI_t, of the two (anti-phase) lines at time t may be calculated from the difference in $\langle I_z(t)\rangle$ obtained with the variation of the sign in $\langle 2I_zS_z(0)\rangle$term. It may be shown that the initial intensity, denoted by I_0, of the individual spectral line in the anti-phase doublet is directly proportional to $(\gamma_H/\gamma_C)\langle S_z(\infty)\rangle$ $(=\hbar\omega_I/(4kT))$. Both the following experimental and calculated results are expressed in terms of differential intensity ratio $\Delta I_t/I_0$.

EXPERIMENTAL

The measurement of $2I_ZS_Z$ spin order have been performed for the carboxyl carbon of methyl formate ($HCOOCD_3$) which was prepared by the esterification of formic acid in excess methanol-d_4 with the presence of trace sulfuric acid. A 15 vol. % solution in methanol-d_4 was sealed in vacuo in a 10 mm tube after three freeze-pump-thaw cycles. Carbon-13 spectra were measured at 273 K with a Bruker MSL-300 spectrometer operating at 7.05 T after 48 scans with a relaxation delay of 150 s set for each scan.

RESULTS AND DISCUSSION

In the following calculation, r=1.101 Å is taken as the proton-carbon internuclear distance in methyl formate[12]. The principal values of the carboxyl shielding tensor in methyl formate are obtained from the solid state powder spectra. Their values are $\sigma_{11} = -90.5$ ppm, $\sigma_{22} = 29.1$ ppm and $\sigma_{33} = 61.5$ ppm with respect to the isotropic shift[13].

The measured $\Delta I_t/I_0$ versus evolution time t is shown in Fig. 1. The theoretical curve is also shown

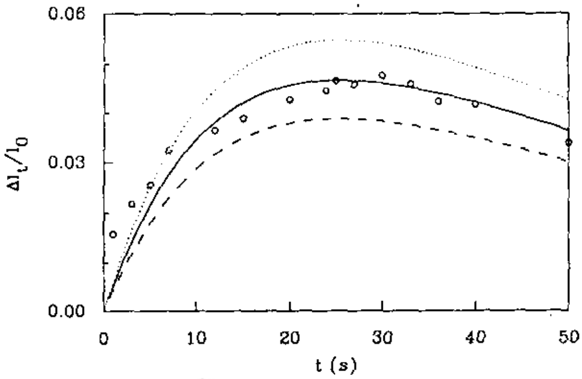

Fig. 1 The variaition of differential intensity ratio $\Delta I_t/I_0$ as a function of evolution time t for $HCOOCD_3$ (15% v/v) in methanol-d_4 solution at 273 K. With τ_c=2.7 ps, dotted, solid and dashed curve are calculated for $\theta_{xz'}$= 134°, $\theta_{xz'}$=132° and $\theta_{xz'}$=130°, respectively.

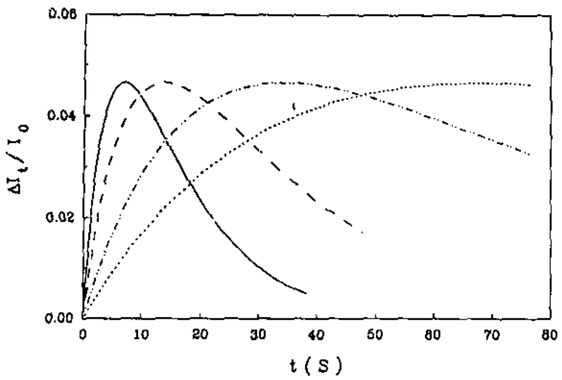

Fig. 2 Plots of calculated differential intensity ratio $\Delta I_t/I_0$ as a function of evolution time t for $\theta_{xy'}$=132° and τ_c= 10, 5, 2, and 1 ps. represented by curves ———, — — —, — · · · —, and · · · · · · · ·, respectively.

in the figure for comparison. In the profile of differential intensity ratio, the experimental maximum intensity appears at around 25–30 s. Since the locus of maximum differential ratio is insensitive to the variation of CSA parameters, and increasing the magnitude of τ_c results in a shift of maximum intensity to a shorter time with an early decay profile (cf Fig. 2), τ_c may be dtermined without the exact knowledge of CSA parameters. More importantly, the magnitude of differential intensity ratio are rather sensitive to the variations of $\theta_{xz'}$ values. Without the CSA-DD cross term, the calculated signal intensity of $2I_zS_z$ spin order is found to vanish. Thus the variation of the differential intensity ratio in the relaxation processes of $2I_zS_z$ spin order demonstrated the importance of cross correlation in ^{13}C–^1H interactions.

It is found that the most shielded element of the tensor, σ_{33}, is nearly parallel to the normal to the COO-plane[14]. The orientations of σ_{11} and σ_{22} axes are much more sensitive to the local structure around the carboxyl group. It appears that increasing the double bond character of C–O bond moved σ_{22} closer to the C–O direction. In ammonium hydrogen malonate, acetic acid and dimethyl oxalate, the σ_{22} component is found at 5°, 12° and 14° off the C=O bond. In the limiting case of the symmetrical ketone benzophenone, σ_{22} is parallel to the C=O bond. Therefore, assignment of σ_{11} to σ_x, σ_{22} to σ_z and σ_{33} to σ_y may be made[14]. In this work, $\theta_{yz'}$=90° is used and the best fit for experimental-values with theoretical calculations may be obtained with τ_C=2.7±0.2 ps and $\theta_{xz'}$=48°±2° or 132°±2° which are consistent with previous results[8]. From single crystal NMR study, $\theta_{yz'}$=89° and $\theta_{xz'}$=133° have been obtained for acetic acid[14] and, recently, Cornell found that σ_{22} is along the C=O bond, and σ_{11} lies in the COO-plane for dimethyl oxalate[15]. This orientation corresponds to $\theta_{xz'}$=145°. Therefore, $\theta_{xz'}$=132°±2° has been chosen as the orientation for the C–H axis relative to the principal x axis of carboxyl shielding tensor for methyl formate. The result showed excellent agreement with the study of Jaccard et al. using the pulse sequence designed for enriched carbon-13 sample at the same temperature[8]. More accurate determination of tensorial orientation of CSA interaction requires detailed studies of temperature-dependent relaxation process which are underway in our laboratory and will be published elsewhere.

This preliminery study showed that the use of coherence transfer to enhance signal in the relaxation of heteronuclear two spin order can be useful for the determination of the orientation between the C–H axis and the principal axis of carboxyl shielding tensor in a liquid sample with natural abundant nuclei.

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