

Relaxation Studies of $2I_zS_z$ Spin Order in Liquid Benzene: Selection of Chemical Shift Anisotropy Parameters

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The effects of cross-correlation of chemical shift anisotropy and dipole-dipole interactions result in the relaxation of $2I_zS_z$ spin order. The intensity of relaxation profile is sensitive to the variation of chemical shift anisotropy interactions. With spin-rotation interaction taken into consideration, it has been successfully applied to the selection of appropriate sets of chemical-shift anisotropy parameters for benzene.

INTRODUCTION

The nuclear-magnetic-resonance relaxation method has been utilized to investigate the molecular dynamics in liquids. Recently, the theory of differential line broadening has been applied to the study of the cross relaxation between chemical shift anisotropy (CSA) and dipole-dipole (DD) interactions.^{1,3} However, the differential line-broadening effects depend on the correlation time of the system for slow motions. For those effects to be experimentally observable, this requirement limits the systems suitable for such study. It may be circumvented by use of selective conversion of Zeeman order into heteronuclear two-spin order (e.g. $2I_zS_z$) of the C-H moiety⁴ to measure those cross correlations in the rapid motional region, and particularly for small molecular systems. With the coherence transfer technique,⁵ it may be applied to regular samples without specific carbon-13 labeling. The relaxation of two-spin order has been invoked in the determination of tensorial parameters of chemical shift anisotropy interactions for methyl formate, and the temperature-dependent relaxation profiles have been studied to examine the importance of spin-rotation interaction.⁷

In the present work, we have examined spin relaxations in liquid benzene. Two sets of tensorial parameters of chemical shift anisotropy interaction of benzene have appeared in the literature.⁸⁻¹¹ To obtain more definite information about the selection of the appropriate set of CSA parameters one may compare the calculated relaxation behavior with experiment. The use of the relaxation study of $2I_zS_z$ spin order is particularly suitable for this purpose as the cross relaxation of CSA and DD interactions gives rise

to the signal of two-spin order.

THEORY

The pulse sequence used for measurement of the relaxation of the $2I_zS_z$ spin order has been presented previously.^{6,7} It basically invokes a coherence transfer sequence as the initial preparation of the spin system:

$$\left(\frac{\pi}{2}\right)_x^H - 1/(2J_{C-H}) - \left(\frac{\pi}{2}\right)_\phi^H - t - \left(\frac{\pi}{2}\right)_y^C - (\text{FID})$$

Here the spin-spin coupling constant J_{C-H} is expressed in Hz. The first two proton 90° pulses are used to generate $^1\text{H} \rightarrow ^{13}\text{C}$ coherence-transfer and the last 90° pulse of ^{13}C converts the signal of two-spin order for observation. The initial density matrix just after the preparation of the spin system with coherence transfer⁵ is given by

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

where ω_S and ω_I are the Larmor frequencies of ^{13}C (denoted as S spin) and ^1H (denoted as I spin) nuclei, respectively. The \pm 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 of spectral lines is observed. As expressed in Eq. 1, the difference in the intensity of the two (anti-phase) lines is related to the evolution of the $2S_z I_z$ terms.

The description of the relaxation processes during time t in which the $2I_zS_z$ coherence evolves is described by

Dedicated to Professor Yau-Tang Lin (林耀堂) on the occasion of his eightieth birthday.

the Redfield theory¹² including the CSA interaction at ¹³C nuclei and the DD interaction between ¹³C and ¹H. To account for the NMR relaxation processes, one describes the populations of an IS system with two nonequivalent spin-1/2 nuclei by the density matrix operator or in terms of the expectation values of the three operators I_z , S_z and $2I_zS_z$.¹³⁻¹⁴ The equation of motion has been given explicitly for the ¹³C-¹H spin system with axially symmetric shielding tensor by Bain and Lynden-Bell¹³ and was later modified for the general asymmetric shielding tensor by Jaccard et al.⁴ Including SR relaxation for ¹³C, it becomes

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

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

$$\begin{aligned} A &\equiv -(10/3)J_{IS,IS} \\ B &\equiv -(10/3)J_{IS,IS} - 4J_{S,S}J_{SR} \\ C &\equiv -2J_{IS,IS} - 4J_{S,S}J_{SR} \\ D &\equiv -(5/3)J_{IS,IS} \\ E &\equiv -4J_{IS,S} \end{aligned} \quad (3)$$

Here $J_{IS,IS}$, $J_{S,S}$, J_{SR} and $J_{IS,S}$ represent the spectral density functions for the DD, CSA, SR and DD-CSA cross relaxations, respectively. For simplicity, we consider only the extreme narrowing condition, e.g., $\omega\tau_c \ll 1$ and $\omega\tau_j \ll 1$ where τ_c and τ_j are the effective reorientation correlation time and the effective angular momentum correlation time of the molecules considered. Other relaxation mechanisms such as remote intramolecular and intermolecular DD interactions are neglected. Thus, the spectral density functions become simplified into the following expressions:

$$\begin{aligned} J_{IS,IS} &\equiv (3/10)\gamma_I^2\gamma_S^2h^2r^{-6}\tau_c \\ J_{S,S} &\equiv (1/30)(\gamma_S B_0)^2 L(\sigma)\tau_c \\ J_{IS,S} &\equiv -(1/20)\gamma_I\gamma_S^2hr^{-3}B_0K(\sigma,\theta_{xz'},\theta_{yz'})\tau_c \end{aligned} \quad (4)$$

Here r is the proton-carbon internuclear distance and the DD relaxations from protons in meta positions of the benzene ring are also included in the $J_{IS,IS}$ term. We also define

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

and

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

in which σ_x , σ_y and σ_z are the principal components of the shielding tensor. The angles $\theta_{xz'}$, and $\theta_{yz'}$, define the relative orientation between the IS internuclear vector (¹H-¹³C) with respect to the principal axes x and y of the σ tensor, respectively. The spectral density function for ¹³C SR relaxation¹⁵ is represented by

$$J_{SR} = (2IkT/h^2)C_{\text{eff}}^2\tau_j \quad (6)$$

where $I = (I_1 + I_2 + I_3)/3$ is the averaged moment of inertia of the molecule, and C_{eff} is the effective SR coupling constant of ¹³C nuclei, expressed in Hz. Because we have considered that the relaxation of reorientational motions of benzene at the temperature near its freezing point is in the Markovian limit ($\tau_c \gg \tau_j$), a generalized Hubbard relation¹⁶⁻¹⁷ holds between the effective reorientational correlation time τ_c and τ_j , i.e.,

$$\begin{aligned} \tau_c &\equiv \tau_c^{(2,0)} [(3\cos^2\theta - 1)/2]^2 + \tau_c^{(2,1)} [3\sin^2\theta \cos^2\theta] \\ &\quad + \tau_c^{(2,2)} [3\sin^4\theta]/4 \end{aligned} \quad (7)$$

θ ($= 90^\circ$) is the angle between the molecular axis and the ¹³C-¹H axis, and $\tau_c^{(j,k)}$ may be evaluated from the following relation:

$$[\tau_c^{(j,k)}]^{-1} = [(j(j+1) - \kappa^2)/I_{\perp} + \kappa^2/I_{\parallel}]kT\tau_j \quad (8)$$

in which we define $I_{\parallel} \equiv I_3$ and $I_{\perp} \equiv I_1 = I_2$.

The effective reorientational correlation time is obtained from the measurement of deuteron relaxations in the system of C₆D₃H₃-C₆D₆. Its relaxation mechanism is due mainly to the electric quadrupolar interactions. In the limit of motional narrowing, the electric quadrupole spin-lattice relaxation rate of deuterons is given by¹⁸

$$1/T_{1D} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \left(\frac{e^2qQ}{h}\right)^2 \left(1 + \frac{\eta^2}{3}\right)\tau_c \quad (9)$$

Here $I = 1$ is for the deuteron with quadrupole moment Q , eq is the gradient of the electric field strength at the deuterium nucleus and η is the asymmetric parameter

($\eta < 1$ for organic molecules). The values of the quadrupole coupling constant, $(e^2qQ/h) = 180.7$ kHz, and of the asymmetry parameter, $\eta = 0.041$, were found for the deuteron in the benzene system.^{19,20} Furthermore, the electric quadrupolar interactions are modulated by the reorientational motion of the molecules as a whole.

The time-evolution of $\langle \Delta S_z(t) \rangle$ is solved from Eq. 2 with the known values of $\langle \Delta I_x(0) \rangle$, $\langle \Delta S_z(0) \rangle$ and $\langle 2I_x S_z(0) \rangle$ which is calculated from the initial density matrix given in Eq. 1 and the final equilibrium distribution. We obtain $\langle \Delta I_x(0) \rangle = -h\omega_I/4kT$, $\langle \Delta S_z(0) \rangle = 0$ and $\langle 2I_x S_z(0) \rangle = \pm h\omega_I/4kT$.

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

EXPERIMENTAL SECTION

1,3,5-trideuterobenzene (98%) and benzene- d_6 (98%) were purchased from Aldrich Chemical Co. Inc.

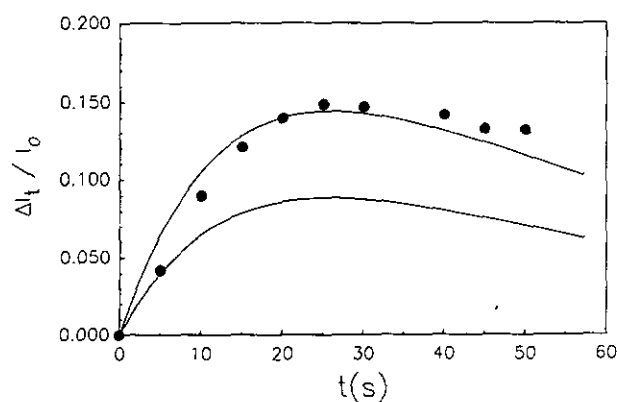


Fig. 1. Plots of the differential intensity ratio $\Delta I_t/I_0$ as a function of evolution time t in benzene- d_6 solution of 1,3,5-trideuterobenzene at 281 K. The upper curve was calculated with CSA parameters due to Linder et al. (ref. 11) whereas lower curve was calculated with CSA parameters due Pines et al. (ref. 10)

The measurements of $2I_x S_z$ spin order have been performed for carbon nuclei of 1,3,5-trideuterobenzene. A 9 vol. % solution in benzene- d_6 was sealed in vacuo in a 10 mm tube after three freeze-pump-thaw cycles. All measurements were obtained with a Bruker MSL-300 spectrometer operating at 7.05 T. Carbon-13 spectra were measured at various temperatures after 48 scans with a relaxation delay 200 s or more set for each scan. The temperatures were controlled within $\pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

In the following calculation, the proton-carbon internuclear distance in benzene²¹ is taken to be $r = 1.1$ Å. The orientation of the principal axis of the carbon shielding tensor in benzene is obtained from solid state powder spectra. The most shielded element of the tensor is believed to be perpendicular to the benzene plane, and the least shielded component is along the C-H axis. Pines et al.¹⁰ obtained $\sigma_{11} = -62.5$ ppm, $\sigma_{22} = -62.5$ ppm and $\sigma_{33} = 117.5$ ppm with respect to the isotropic shift at 223 K whereas Linder et al.¹¹ obtained $\sigma_{11} = -88.2$ ppm, $\sigma_{22} = -12.0$ ppm and $\sigma_{33} = 127.7$ ppm at 14 K. We identify σ_{11} with σ_x , σ_{22} with σ_z , and σ_{33} with σ_y in relaxation equations.

The moment of inertia for 1,3,5-trideuterobenzene has been calculated from the structural data.²¹ We obtain $I_1 = 163.1 \times 10^{-40}$ g cm², $I_2 = 163.1 \times 10^{-40}$ g cm² and $I_3 = 326.2 \times 10^{-40}$ g cm², I_3 being the component perpendicular to the benzene plane. The spin-rotation coupling parameter $C_{\text{eff}} = 1.602$ kHz was obtained experimentally from the relaxation study of ¹³C in gaseous benzene.²²

The measurements of deuteron relaxation rates at 281 K gives $T_{1D} = 1.08$ s. This corresponds to an effective reorientational correlation time $\tau_c = 1.93$ ps. The measured $\Delta I_t/I_0$ values versus evolution time t at 281 K are shown in Fig. 1. With the measured effective reorientational correlation time and the τ_i values calculated from the Hubbard relation, the theoretical curves calculated from two different sets of CSA parameters are also displayed in the same figure for comparison. The parameters obtained by Linder et al. fit the experiments better than the parameters obtained by Pines et al. The former CSA parameters result in more than double the enhancement of the magnitude of the cross correlation term and thus a larger intensity of two-spin order, relative to the latter CSA set which shows a non-negligible deviation of relaxation in-

tensity of the two-spin order from experiment. It is also evident that from molecular dynamics calculation rotation around C_6 axis is only slightly hindered in solid benzene at 261 K as compared to the motion in the liquid state.²³ Internal motions of many types are considered to be immobilized at temperatures below 77K.¹¹ Therefore motion about C_6 -axis may still be significant in the work of Pines et al. For this reason their CSA parameters are pre-averaged over internal rotations. They may not be utilized to represent the true tensorial components of CSA interactions.

CONCLUSION

In the literature, distinct sets of CSA parameters are commonly given for the same molecule. The differences are attributed to the effects of internal molecular rotation. It has been demonstrated that relaxation studies of $2I_2S_z$ spin order may be used to select an appropriate set of CSA parameters. Other methods such as differential recovery of proton coupled ^{13}C lines may also be applied to the study of cross relaxation. An investigation along this line is under way in our laboratory.

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Key Words

$2I_2S_z$ Spin order; Chemical shift anisotropy interaction.

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