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A Study on Spin-Lattice Relaxation of ^{19}F Spins in Benzotrifluoride: Contributions from Dipole-Dipole Interaction and Spin-Rotation Interaction

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In this work we have studied the spin-lattice relaxation of ^{19}F spins in benzotrifluoride in our quest for a reliable method of discriminating the contribution due to dipolar relaxation mechanism from that due to spin-rotational mechanism for nuclear spins located on methyl or substituted methyl group in organic molecules. Over the temperature range of 248-268 K the decay of normalized longitudinal magnetization was found to be well described by a two-parameter equation of the form

$$R(t) = \exp(-st) \left\{ \frac{5}{6} \exp(-s_1 t) + \frac{1}{6} \right\}$$

which was derived under the assumption that interactions in the A_3 spin system are modulated randomly and predominantly by internal rotational motions of $-\text{CF}_3$ top, and it was shown that the separation of contribution due to dipolar interactions from that due to spin-rotation interaction could be successfully achieved by least-square fitting of observed data to this equation. The results indicate that the spin-rotational contribution is overwhelmingly larger than that of dipolar origin over the given temperature range and becomes more dominating at higher temperature.

Introduction

Study of the magnetic relaxation mechanisms for a nuclear spin (or spins) located on a molecule often yields invaluable information regarding the dynamics of this molecule in bulk phase.^{1,2} Among several relaxation mechanisms for a nuclear spin (or spins) of $I=1/2$ those due to intra- and intermolecular magnetic dipole-dipole interactions are usually dominant ones, but for a spin (or spins) in a rapidly rotating small molecule or internal rotor such as methyl group the spin-rotation interaction is also known to make appreciable con-

tribution to its (or their) relaxation.³ Study of dipolar mechanism is well known to provide us with the information related to the modulation of internuclear distance vectors whereas that of spin-rotation mechanism unveils the dynamics of modulation of molecular rotational angular momentum vectors.⁴ Therefore, it is important to separate the contribution due to the former from that originating from the latter. Previously, this separation was often achieved in liquid by means of observing the nuclear magnetic relaxation as a function of temperature and then relating this temperature dependence to that of the solvent (or solution) viscosity.^{5,6} However, there has been lingering skepticism, or even criticism, over the use of macroscopic quantities like viscosity

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of the medium to interpret microscopic phenomena such as molecular tumbling, etc. This kind of controversy may be avoided for ^{13}C spins if the NOE data, which are experimentally obtained by means of the gated decoupling technique, are directly used to effect the separation of the two contributions from each other, but, very unfortunately, no such means are available for identical protons such as those on methyl group.⁷ Ostensibly, substitution of protons by deuterium atoms may appear to serve for this purpose, but the results published by Spiess *et al.* indicate that this is not the case for the spins located on a rapidly rotating internal rotor.⁸

In this regard we have recently shown⁹ that a relaxation equation described by Werbelow and Grant for the A_3 spin system¹⁰ can be applied to achieve the desired separation if the parameters involved in this equation are adjusted in such a way that the calculated curve may best fit to the observed relaxation data for protons over a wide range of time. However, our effort has been somewhat hampered by a few nagging questions, such as "under what condition our method can best suit" and "whether this procedure can also be used for other nuclear species such as ^{19}F spins in benzotrifluoride". The main goal of the present research is to provide the answers to these questions as well as to put the rationale behind our approach on firmer footing by observing and interpreting the ^{19}F spin-lattice relaxation in benzotrifluoride.

Theory

The only observable normal (magnetization) mode, v_1 , for the A_3 system comprised of three identical spins is defined as

$$v_1 = \text{Tr}[(I_{1z} + I_{2z} + I_{3z})\chi(t)] \quad (1)$$

where we have used the notations given in ref. 10. The deviation density operator χ , defined as usual by

$$\chi(t) = \sigma(t) - \sigma^T, \quad (2)$$

can be shown to evolve following the equation of motion

$$\frac{d\chi}{dt} = \mathbf{R}\chi, \quad (3)$$

where σ^T indicates the spin density operator at thermal equilibrium and \mathbf{R} the relaxation supermatrix. It can be shown that the time evolution of v_1 mode for this system is coupled with those of two nonobservable modes, v_2 and v_3 , which are defined by

$$v_2 = (4/\sqrt{5})\text{Tr}[\{I_{1z}(I_2 \cdot I_3) + I_{2z}(I_1 \cdot I_3) + I_{3z}(I_1 \cdot I_2)\}\chi(t)] \quad (4)$$

and

$$v_3 = \sqrt{8/15} \text{Tr}[\{15I_{1z}I_{2z}I_{3z} - 3[I_{1z}(I_2 \cdot I_3) + I_{2z}(I_1 \cdot I_3) + \dots]\}\chi] \quad (5)$$

Werbelow and Grant¹⁰ have shown that in the extreme narrowing limit v_3 mode is decoupled from both v_1 and v_2 , and the relaxation equations for the latter two modes become

$$-\frac{d}{dt} \begin{pmatrix} v_1(t) \\ v_2(t) \end{pmatrix} = \begin{pmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{pmatrix} \begin{pmatrix} v_1(t) \\ v_2(t) \end{pmatrix}. \quad (6)$$

The coefficients of coupling between two normal modes v_i and v_j , Γ_{ij} 's, are found to be expressed as

$$\Gamma_{11} = 10J + 2j, \quad \Gamma_{12} = \Gamma_{21} = (10/\sqrt{5})K,$$

and

$$\Gamma_{22} = 4J - 2K + 6j - 4k, \quad (7)$$

where J and K are, respectively, the zero-frequency dipolar auto- and cross correlation spectral densities, and j and k are the zero-frequency random field auto- and cross correlation spectral densities, whose definitions have explicitly been given by Werbelow and Grant. These authors have also shown that the solution for v_1 may be written as

$$R(t) \equiv \frac{v_1(t)}{v_1(0)} = a_+ \exp(-l_+ t) + a_- \exp(-l_- t) \quad (8)$$

where

$$l_{\pm} = [7J - K + 2j + 2(j-k)] \pm \{[3J + K + 2(k-j)]^2 + 20K^2\}^{1/2} \quad (9)$$

and

$$a_{\pm} = \frac{1}{2} \left(1 \pm \frac{3J + K - 2(k-j)}{\{[3J + K + 2(k-j)]^2 + 20K^2\}^{1/2}} \right) \quad (10)$$

Eq. (8) is actually a three-parameter equation because of the constraint $a_+ + a_- = 1$. It is not a straightforward task to extract the information about all of four spectral densities J , K , j , and k , because we can at best determine only three parameters, l_+ , l_- , and a_+ by least-square fitting of Eq. (8) to experimental data. Therefore, it is necessary to introduce an assumption to determine a correct parameter set of J , K , j , and k uniquely, as we have shown in our previous work. Since it is reasonable to assume that the random fields $B(i, t)$'s responsible for the spin-rotational relaxation are completely correlated with each other if these fields are modulated dominantly by internal rotation, we may set, to a good approximation, $j = k$. In this case it can be seen from Eq. (8) that the pre-exponential factors does not involve any spin-rotational terms and the equation itself is simplified to the following factored-out form:

$$R(t) = \exp(-st)[A_1 \exp(-s_1 t) + (1 - A_1) \exp(-s_2 t)], \quad (11)$$

where

$$s = 2j, \quad (12)$$

$$A_1 = \frac{1}{2} \left(1 + \frac{3J \times K}{\{[3J + K]^2 + 20K^2\}^{1/2}} \right) \quad (13)$$

$$s_1 = 7J - K + [(3J + K)^2 + 20K^2]^{1/2}, \quad (14)$$

and

$$s_2 = 7J - K - [(3J + K)^2 + 20K^2]^{1/2}, \quad (15)$$

It is obvious that the bracketed portion on the righthand side of Eq. (11) coincides with the expression for relaxation function of dipolar origin in the A_3 system which was first derived by Hubbard.^{11,12} Thus the factored-out form of the normalized relaxation function $R(t)$ means that we can separate out the spin-rotational contribution from the dipolar part if three parametric values, J , K , and j are determined. The case of complete correlation can occur when the random field at the site of a nuclear spin on a symmetrical internal

rotor such as methyl group arises solely from internal rotation. Earlier, Burke and Chan¹³ pointed out that, as long as temperature is not too high, spin-rotational relaxation of ^{19}F in benzotrifluoride mainly proceeds through the interactions with magnetic fields arising from internal rotation, in which case the approximation $j=k$ is supposed to be well valid. In other cases for which this approximation is not recommendable, however, no such factoring-out is possible and the relaxation function $R(t)$ depends on both dipole-dipole and spin-rotation interactions in a complicated manner. Thus the success of our method relies on whether experimental data can faithfully be reproduced over full range of time by adjusting three parameters J , K , and j involved in Eq. (11). For this purpose the nonlinear least square fitting procedure can be utilized along with the simplex algorithm.

Experimental

α,α,α -trifluorotoluene (benzotrifluoride, 99. + %) purchased from the Aldrich Chemical Co. was used without further purification. This was dissolved in 100% CDCl_3 and the sample solutions were prepared in three different concentrations, 0.189, 0.0842, and 0.0361 M . Each solution was then placed in a carefully cleaned 5 mm o.d. NMR tube. This was degassed by repeating the freeze-pump-thaw cycles five times and then sealed under vacuum (less than 10^{-5} torr). The ^{19}F spin-lattice relaxation data were measured for these samples at 188.22 MHz on a Varian VXR 200S NMR spectrometer over the temperature range of 248-308 K by making use of the typical inversion recovery pulse sequence (delay- 180° - t - 90° -acquire). Temperature variation was performed with the help of temperature controller attached to the spectrometer. In each experiment the probe temperature was regulated to within the accuracy of $\pm 1^\circ\text{C}$, and the pulse delay was taken to exceed $5T_1$ in order to allow the magnetization to be completely restored to thermal equilibrium value before the next 180° pulse is applied. To enhance the reliability of measurements we have maintained the magnetic field homogeneity as uniform and constant as possible employing the autoshim capability provided by our spectrometer throughout the experiments, and M_0 , the equilibrium magnetization, was measured at three different time intervals including $t=0$ and $t=\infty$ (normally taken to be longer than $5T_1$) and their average was used to calculate $\{M_0 - M_x(t)\}/2M_0$ which amounts to $R(t)$ in Eq. (8) when extrapolated to infinite dilution to eliminate the contributions from intermolecular dipolar interactions. Experimental errors in $R(t)$ were estimated to be within $\pm 5\%$.

Results and Discussion

^{19}F spin-lattice relaxation data $R(t)$, free of intermolecular contributions, were obtained by extrapolating the data obtained for three different concentrations to infinite dilution in the same manner as demonstrated in our earlier work⁹ and the results were drawn to semilog scale in Figure 1 through 3. Direct application of the simplex method of nonlinear least-square fitting may yield several sets of parameters each of which corresponds to a local minimum, but only one of them should be the true minimum and thus physically acceptable. Requirement of the smallest standard deviation

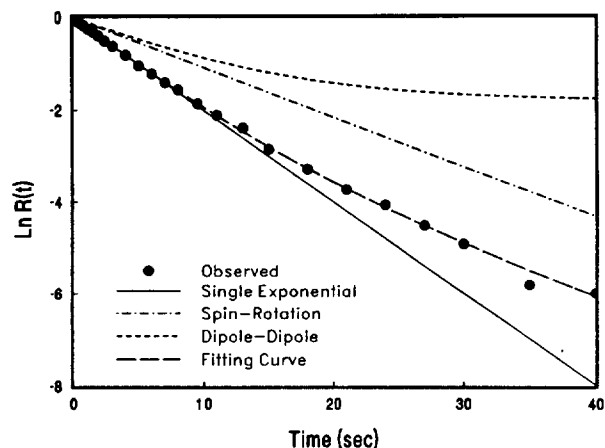


Figure 1. Least-square fitting of $\ln R(t)$ to the observed data at 248 K.

alone may not in general suffice to determine this acceptable set uniquely because there may frequently exist a few viable sets of parameters which can reproduce the observed data to the same degree of precision within experimental errors.¹⁴ In such cases we may need to invoke a few of the following additional requirements which can help us reduce the number of possible candidates. First, the definition of auto-correlation spectral density requires that J can assume only positive value and should be no smaller than the absolute magnitude of K , and secondly, neither s_1 nor s_2 should be negative since the bracketed portion in Eq. (11) induces the decay of magnetization *via* dipolar relaxation. These two conditions should be strictly met and impose some restrictions on the magnitude of K through Eqs. (14) and (15). The third condition emerges from physical considerations rather than mathematical requirements. It comes from the fact that, as shown by Hubbard¹⁵ for the first time, if rotational diffusion about the symmetry axis of methyl or substituted methyl group is much more facile than those about two other axes perpendicular to this symmetry axis, K becomes nearly equal to J . At the same time k may also be assumed equal to j . In this case s_2 becomes vanishingly small and it is evident from Eq. (11) that intramolecular dipolar interactions alone cannot restore the system fully to its previous thermal equilibrium state. Even in this case, however, the presence of other pathways such as the spin-rotational relaxation guarantees the full restoration of the spin system to thermal equilibrium. Although this third condition is not as imperative as the preceding two, we assume that this normally holds for nuclear spins located on a small, symmetrical, rapidly rotating internal rotor in a relatively large asymmetric molecules. If this condition is well met, our problem is actually reduced to an easy two-parameter fitting procedure. The fourth and final consideration is based on the fact that s should be larger than both s_1 and s_2 for a nuclear spin (or spins) whose relaxation is dominated by spin-rotation interactions. For instance, at room temperature or above it was found that the spin-rotation interaction plays a dominant role in the spin-lattice relaxation of ^{19}F in benzotrifluoride, in which case s in Eq. (11) is expected to be larger than both s_1 and s_2 .

In interpreting the ^{19}F relaxation data we have ignored

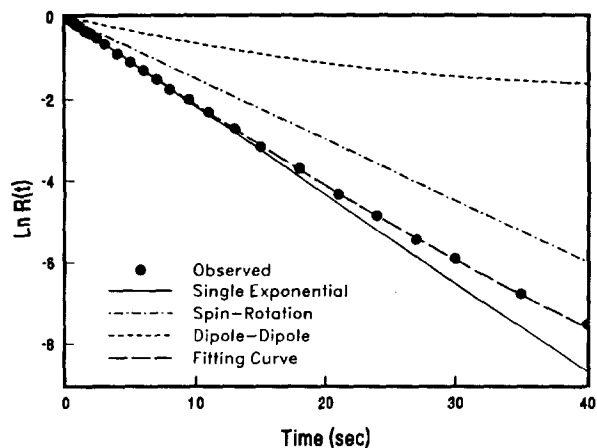


Figure 2. Least-square fitting of $\ln R(t)$ to the observed data at 258 K.

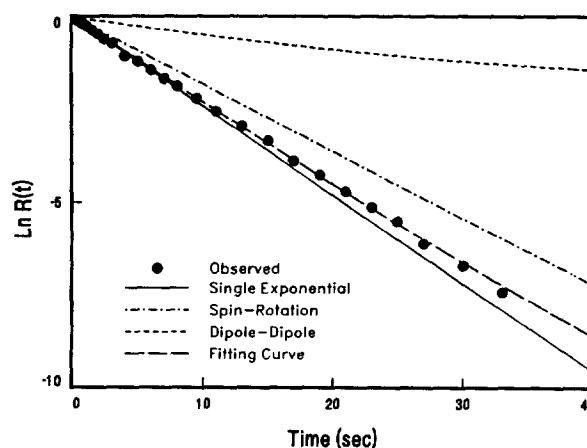


Figure 3. Least-square fitting of $\ln R(t)$ to the observed data at 268 K.

the contribution from intramolecular dipole-dipole interactions between ring protons and fluorine atoms for several reasons. First, the efficiency of dipolar relaxation is known to be proportional to inverse sixth power of internuclear distance multiplied by the product of square of magnetogyric ratios of two interacting spins. The closest distance between a ring proton in *ortho* position and a fluorine nucleus on the $-\text{CF}_3$ group and the interfluorine distance are, respectively, estimated to be about 2.40 and 1.46 Å. Using this structural information along with magnetogyric ratio of each nucleus, we find that dipolar contribution from interaction with *ortho* proton should be no greater than 5.9% of that due to interfluorine interactions. Secondly, it is well known that dipolar interactions among identical spins is known to provide more efficient relaxation pathway than those among non-identical spins, as is well manifested by the so-called 3/2 effect.¹ The third and final reason is that, as was shown by Woessner,¹⁶ F-H interactions become less effective when these interactions are modulated by internal rotation than otherwise. Therefore, the contributions from dipolar interactions with ring protons may be assumed to be negligible. This was confirmed by our experimental observation that there was no noticeable change in fluorine signal intensity when the ring protons were irradiated.

In a preliminary calculation we have found that there exist several sets of optimum values of J , K and j which can reproduce the observed data equally well within experimental errors over the full time range; however, for all these sets J was found to be nearly equal to K . This coincidence is not fortuitous because modulation of interfluorine dipolar interactions in the $-\text{CF}_3$ top is expected to be dominated by internal rotation about the symmetry axis of this top as long as temperature is not too high. These preliminary results have encouraged us to assume $J=K$ for our treatment of fluorine spin-lattice relaxation in benzotrifluoride. With this assumption Eq. (11) becomes

$$R(t) = \exp(-st) \left\{ \frac{5}{6} \exp(-s_1 t) + \frac{1}{6} \right\}, \quad (16)$$

where

$$s = 2j \text{ and } s_1 = 12 J \quad (17)$$

Table 1. Spectral Densities Determined by Minimizing the Square Deviation Given by Eq. (18) (all the values are expressed in unit of sec^{-1})

	248 K	258 K	268 K
J	0.00988	0.00694	0.00506
j	0.0538	0.0746	0.0906
Standard deviation	0.0265	0.0193	0.0374

The parameters j and J have been determined by minimizing the following square deviation

$$\sum_i \{ \ln R_i - \ln R(t_i) \}^2 \quad (18)$$

and the results are presented in Figure 1 through 3 and in Table 1. These results show that over temperature range of 248-268 K the spin-lattice relaxation of ^{19}F in benzotrifluoride can be described very well by Eq. (16), which justifies our assumption that $j=k$ and $J=K$. As temperature goes up, j increases while J diminishes rapidly, thus making the spin-rotation term more and more dominant. Beyond room temperature we found that $R(t)$ were almost exponential, in which case the contribution comes exclusively from the spin-rotation term. Of course, one will worry about the possibility that the assumption $j=k$ and $J=K$ may break down at higher temperature. In this case, however, both J and K become so small, compared to j and k , that any deviation from our proposed model can hardly be observed, but the approximation $j \cong k$ can surely be violated because, as temperature goes up, end-over-end (overall) molecular rotation will make more and more contribution to the random field $B(i, t)$ as was demonstrated by Burke and Chan.¹³ However, even in this case $R(t)$ can take the single exponential form as long as j is far greater than $j-k$, as can easily be seen from Eq. (8).

Glasel *et al.*¹⁷ have reported that they were unable to describe the spin-lattice relaxation of methyl protons in aqueous amino acid solutions even by a full four-parameter fitting based on an equation similar to Eq. (8). In this context we would like to point out that these authors failed to note that Eq. (8) is valid only for the case where the extreme

narrowing condition can be satisfied. For a rodlike chain molecule like amino acids in a viscous medium such as aqueous solution this condition will not in general be satisfied very well, and then all three modes ν_1 , ν_2 , and ν_3 may remain coupled to one another. This in turn will give the solution $R(t)$ as a combination of three exponential terms, which explains why the combination of only two exponential terms failed to explain the relaxation of methyl protons in this case. Only way to get out of trouble in this situation is to treat the methyl group as an A_3X system, including ^{13}C besides three protons, and obtain the data for as many observable modes as possible. Application of this technique to a few examples is under investigation in our laboratory.

Concluding Remarks

It was found that at room temperature or below the spin-lattice relaxation of ^{19}F in benzotrifluoride could be well described by a two-parameter equation given explicitly in Eq. (16) which was derived under the assumption that modulation of interactions in the spin system, both dipole-dipole and spin-rotation, is caused predominantly by internal rotational motions in the molecule, and the separation of contribution due to dipolar interactions from that due to spin-rotation interaction was successfully achieved by least-square fitting of observed data to this equation. As expected, the spin-rotational contribution was found to overwhelm that of dipolar origin over the temperature range of 248-268 K and becomes more dominating at higher temperature.

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Transition Rates in a Bistable System Driven by Singular External Forces

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A noise-induced transition is presented for a bistable system subjected to a multiplicative random force, which is singular at the unstable state. The stationary probability distribution is obtained from the Fokker-Planck equation and the effects of the singularity is analyzed. On the basis of noise-induced phase transition with Gaussian white noise, the relaxation time and the transition rate of the system are evaluated up to the first order correction of D . In the parameter region $\nu < 1$, the transition rates decrease as the exponent ν goes to 1 and as the coefficient of the linear term of the kinetic equation increases.

Introduction

In recent years there have been increasing interests in

the investigation of the dynamic properties in the fluctuating nonlinear system. In particular, a number of papers have been devoted to the study of relaxation times (or mean first-passage times) and transition rates in bistable systems driven by random forces¹⁻³. Depending on the properties of the

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