Nuclear Magnetic Relaxation by Anisotropy of the Chemical Shift

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Introduction

The problem of nuclear magnetic relaxation in the laboratory frame in the presence of anisotropy of the chemical shift has been considered in a series of papers 1-7. In the previous papers it was assumed that the chemical shift tensor is a symmetric one, but there are some theoretical suggestions that generally the chemical shift tensor may be unsymmetric with nine independent elements 8,9. Unfortunately, only the symmetric part of the tensor is accessible through measurements of NMR spectra 10. However, the antisymmetric part of the anisotropy of the chemical shift can contribute to the relaxation rate in the presence of molecular reorientations.

The purpose of this paper is to calculate the resultant relaxation rate due to the symmetric and antisymmetric part of the anisotropy of the chemical shift both in the laboratory and rotating frame. The calculations are performed in a weak collision case using a method presented elsewhere 11.

Theory

Consider a system of nuclear spins I in the presence of a strong external magnetic field $H_0$ along the z-axis in the laboratory frame. The Hamiltonian $H$ may be written as a sum of two terms, the Zeeman term and the chemical shift term:

$$H = -\hbar \gamma I \cdot (1 - \sigma) \cdot H_0 = -\hbar \gamma I \sum_{pq} (\delta_{pq} - \sigma_{pq}) H_{0y} I_p,$$

(1)

where $\sigma_{pq}$ is the chemical shift tensor (screening tensor), $\delta_{pq}$ is Kronecker’s delta, $I_p$ are components of nuclear spin, $H_{0y} = H_0 \delta_{pq}$ are the components of the field $H_0$ in the laboratory frame, and $\gamma$ is the gyromagnetic ratio for the nucleus considered. In our present consideration we ignore spin-spin interactions discussed previously 11,12. The Hamiltonian given by the Eq. (1) may be presented as a contraction of two cartesian tensors of the second rank, namely:

$$G = \sum_{pq} T_{pq} A_{qp},$$

(2)

$$T_{pq} = (\sigma_{pq} - \delta_{pq}) \omega_0 \equiv (\sigma_{pq} - \delta_{pq}) \gamma I H_0,$$

(3)

$$A_{qp} = n_{0q} I_p \equiv (H_{0q}H_0) I_p,$$

(4)

where $\omega_0$ is the Larmor precession angular frequency and $n_0$ is a unit vector along the $H_0$ field.

The tensors $T_{pq}$ and $A_{qp}$ may be reduced into the irreducible spherical tensors $F_{lm}$ and tensor operators $A_{lm}(I, n_0)$ of orders $l = 0, 1, 2$, respectively (l.c. 11,13-15) and finally the Hamiltonian (1) may be written in the following general form:

$$G = \sum_{l=0}^{2} \sum_{m=-l}^{l} (-1)^m A_{lm}(I, n_0) F_{l-m},$$

(5)

where in the laboratory frame one gets

$$A_{00}(I, n_0) = I \cdot n_0 = I_z,$$

(6)

$$A_{10}(I, n_0) = -\frac{1}{\sqrt{2}} (I_z n_x - I_x n_z) = 0,$$

(7)

$$A_{11}(I, n_0) = -\frac{1}{\sqrt{2}} (I_z n_x - I_x n_z) = -\frac{1}{\sqrt{2}} I_x,$$

(8)

$$A_{20}(I, n_0) = I_x n_z - \frac{1}{4} (I_x n_x + I_y n_y) = I_z,$$

(9)

$$A_{21}(I, n_0) = \frac{1}{4} (I_x n_x + I_y n_y) + I_x = \frac{1}{4} I_z,$$

(10)

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\[ A_{2 \pm 2}(I, n_0) = \frac{\sqrt{6}}{4} I_+ n_+ \equiv \frac{\sqrt{6}}{4} \]
\[ (I_+ \pm i I_y)(n_+ \pm i n_y) = 0, \quad (11) \]
\[ F_{00} = \frac{1}{2} \sum_p T_{pp} \equiv -\omega_0 (1 - \sigma), \quad (12) \]
\[ F_{10} = -\frac{i \omega_0}{2} (\sigma_{xy} - \sigma_{yx}), \quad (13) \]
\[ F_{1 \pm 1} = \frac{\omega_0}{2\sqrt{2}} \left[ (\sigma_{xx} - \sigma_{xx}) \pm i (\sigma_{yz} - \sigma_{zy}) \right], \quad (14) \]
\[ F_2 = \omega_0 (\sigma_{zz} - \sigma), \quad (15) \]
\[ F_{2 \pm 1} = \frac{\omega_0}{\sqrt{6}} \left[ (\sigma_{xx} + \sigma_{zz}) \pm i (\sigma_{yx} + \sigma_{zy}) \right], \quad (16) \]
\[ F_{2 \pm 2} = \frac{\omega_0}{\sqrt{6}} \left[ \sigma_{xx} - \sigma_{yy} \pm i (\sigma_{xy} + \sigma_{yx}) \right], \quad (17) \]

where \( \sigma = \frac{1}{3} \text{Tr} \sigma \) is the ordinary screening constant.

In the presence of molecular reorientations the spherical tensors \( F_{1m} \) and \( F_{2m} \) are random functions of time and the terms \( G^{(1)} \) and \( G^{(2)} \) of the Hamiltonian (5) can contribute to the relaxation rate.

\[
\frac{1}{T_{N_0}} = \sum_{i=0}^{2} \frac{1}{T_{N_i}} = \frac{1}{12} \sum_{i=0}^{2} \sum_{m=-i}^{i} 12 \, c_i \left( \frac{l}{m-N+1} \right)^{12} \left( \frac{l}{m-N+1} \right)^{l} \left( \frac{l}{m-N+1} \right)^{l} \frac{d^{(1)}_{m n} (\beta)}{1 + (m \omega + m^* \omega_0)^2 \tau_{cl}^2}, \quad (N = 1, 2), \quad (18) \]

where
\[
c_0 = \frac{1}{3} (\delta \omega)^2, \quad (19) \]
\[
c_1 = \frac{1}{2} \omega_0^2 (\delta \omega)^2 \equiv \frac{1}{2} \omega_0^2 [(\sigma_{xy} - \sigma_{yx})^2 + (\sigma_{zz} - \sigma_{zz})^2 + (\sigma_{yy} - \sigma_{zz})^2], \quad (20) \]
\[
c_2 = \frac{1}{2} \omega_0^2 (\delta \omega)^2 \equiv \frac{1}{2} \omega_0^2 \left\{ (\sigma_{xx} - \sigma_{xx})(\sigma_{xx} - \sigma_{yy}) + (\sigma_{zz} - \sigma_{zz})(\sigma_{zz} - \sigma_{zz}) \right\} + \frac{1}{8} \left\{ (\sigma_{xx} + \sigma_{yy})^2 + (\sigma_{xx} + \sigma_{zz})^2 + (\sigma_{yy} + \sigma_{zz})^2 \right\}, \quad (21) \]
\[
\omega_0 = \gamma_1 H_e = \sqrt{(\omega_0 - \omega)^2 + \omega_1^2}, \quad (22) \]
\[
\omega_1 = \gamma_1 H, \quad (23) \]
\[
\beta = \text{arc tan}[\omega_1/(\omega_0 - \omega)], \quad (24) \]

From the above formulas one can get as a special case the known expressions for the relaxation times \( T_1 \) and \( T_2 \) in the presence of the symmetric part of the chemical shifts \( \delta \sigma \) and the expression for \( T_{1 \sigma} \) in the presence of spin exchange for chair-to-chair isomerization \( \tau_0 = \tau_\sigma \). Moreover, one can get also the relaxation contributions to \( T_1 \) and \( T_2 \) due to the antisymmetric part \( G^{(1)} \) of the chemical shift anisotropy in the laboratory frame and the relaxation contributions to \( T_{1 \sigma} \) and \( T_{2 \sigma} \) due to the symmetric and antisymmetric part of the chemical shift anisotropy. In the case of isotropic molecular reorientations, when \( \tau_{cl} = \tau_\sigma = \tau_0 \) and under normal resonance conditions \( \omega = \omega_0, \beta = \pi/2, \omega_1 \ll \omega_0 \) it follows that:

Moreover, in the case of spins exchanging positions between two sites with chemical shifts \( + \delta \omega/2 \) and \( - \delta \omega/2 \) from \( \omega_0 \), also the term \( G^{(0)} \) can provide a relaxation mechanism \( \tau_0 = \tau_\sigma \). Using the method presented elsewhere \(^{11}\) and well known commutation relations and transformation properties for the tensor operators and spherical tensors respectively, one can calculate the relaxation rate due to the chemical shifts in both the laboratory and rotating frame. The calculations were performed under the assumption that correlation times \( \tau_{cl} \) for the interactions \( G^{(1)} \) are much shorter than the spin-spin relaxation time in a rigid lattice (weak collision approach).

In the case of the relaxation in rotating frame (RF) one has to take into account the radiofrequency field \( 2 H_1 \cos \omega t \) perpendicular to \( H_0 \), which gives an effective component \( H_1 \) along the x-axis of the RF. As a result of the calculation one can get the following expression for the relaxation times \( T_{1c} \) and \( T_{2c} \) in the RF:

\[
T_{N_0} = \frac{1}{2} \sum_{i=0}^{2} \frac{1}{T_{N_i}} = \frac{1}{12} \sum_{i=0}^{2} \sum_{m=-i}^{i} 12 c_i \left( \frac{l}{m-N+1} \right)^{12} \left( \frac{l}{m-N+1} \right)^{l} \left( \frac{l}{m-N+1} \right)^{l} \frac{d^{(1)}_{m n} (\beta)}{1 + (m \omega + m^* \omega_0)^2 \tau_{cl}^2}, \quad (N = 1, 2), \quad (18) \]

where \( d^{(1)}_{m n} (\beta) \) is the transformation matrix for rotation around y-axis through the angle \( \beta \) between the direction of \( H_0 \) field and the effective field \( H_1 \) in the RF \(^{11,15}\), \( \delta \sigma \) and \( \Delta \sigma \) are the asymmetry and anisotropy parameters for the screening tensor \( \sigma_{pq} \) in the molecular reference frame, respectively. From Eq. (18) one can get directly the general expressions for the spin-lattice and spin-spin relaxation times \( T_1 \) and \( T_2 \) in the laboratory frame, respectively:

\[
\left( \frac{1}{T_{N_0}} \right)_{\omega_0 = \beta = 0} = \frac{1}{T_{N}}, \quad (N = 1, 2), \quad (25) \]

where \( d^{(1)}_{mn} (0) = \delta_{mn} \).
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\[ T_{1\rho} = \frac{(\delta \omega)^2}{4} \frac{\tau_c}{1+\omega^2 \tau_c} + \frac{\omega^2 (\Delta \sigma)^2}{4} \frac{\tau_c}{1+9 \omega^2 \tau_c^2} \]  
\[ + \frac{\omega^2 (\Delta \sigma)^2}{45} \tau_c \left( \frac{4}{1+\omega^2 \tau_c^2} + \frac{3}{1+9 \omega^2 \tau_c^2} \right), (26) \]

\[ T_{2\rho} = \frac{(\delta \omega)^2}{8} \frac{\tau_c}{1+\omega^2 \tau_c^2} + \frac{3 \omega^2 (\Delta \sigma)^2}{8} \tau_c \]  
\[ + \frac{\omega^2 (\Delta \sigma)^2}{90} \tau_c \left( \frac{4}{1+\omega^2 \tau_c^2} + \frac{9}{1+9 \omega^2 \tau_c^2} \right), (27) \]

Also the relaxation times \( T_1 \) and \( T_2 \) may be easily expressed in explicit form, namely:

\[ T_1 = \frac{\omega^2 (\Delta \sigma)^2}{2} \frac{\tau_c}{1+9 \omega^2 \tau_c^2} + \frac{2 \omega^2 (\Delta \sigma)^2}{15} \tau_c \]  
\[ (28) \]

\[ T_2 = \frac{(\delta \omega)^2}{4} \tau_c + \frac{\omega^2 (\Delta \sigma)^2}{4} \tau_c \frac{1+9 \omega^2 \tau_c^2}{1+9 \omega^2 \tau_c^2} \]  
\[ + \frac{\omega^2 (\Delta \sigma)^2}{45} \tau_c \left( \frac{4}{1+\omega^2 \tau_c^2} + \frac{3}{1+9 \omega^2 \tau_c^2} \right), (29) \]

One can note that for sufficiently low field \( H_1 \) one gets \( T_{1\rho} = T_2 \). In the extreme narrowing case it follows from Eqs. (26) – (29) that \( T_1 = T_2 \) and \( T_1 = T_2 \) and under appropriate conditions it may be even possible to find \( T_1 < T_2 \) if \( (\delta \omega)^2 > \frac{4}{45} (\Delta \sigma)^2 \) and \( \delta \omega = 0 \).

It has been found experimentally that the symmetric part of the chemical shift anisotropy can play an important role in nuclear magnetic relaxation in the laboratory frame for \(^{19}\text{F}, ^{13}\text{C}\) and \(^{31}\text{P}\) \(^4-7\). It seems that investigation of the field dependence of \( T_1, T_2, T_{1\rho} \) and \( T_{2\rho} \) may be a basis for discovery of the antisymmetric part of the screening tensors which is unobservable in NMR spectra.

In the considerations presented we have neglected relaxation contributions due to the spin-spin interaction calculated previously \(^{11,12}\). One has to note that there are time correlations between the spin-spin interaction and the anisotropy of the chemical shifts leading to an interference effect in nuclear magnetic relaxation in the laboratory frame \(^{17}\). Such interference effects should appear also in the rotating frame. This problem will be considered elsewhere.

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