Nuclear Magnetic Relaxation by Anisotropy of the Chemical Shift

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(Z. Naturforsch. **27 a**, 1456—1458 [1972]; received 27 July 1972)

The relaxation times T_1, T_2, $T_{1\varrho}$ and $T_{2\varrho}$ are calculated in the weak collision case in the presence of anisotropy of the chemical shifts.

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 $\mathcal{H}$ may be written as a sum of two terms, the Zeeman term and the chemical shift term:

$$\begin{aligned}\mathcal{H} \equiv \hbar G = -\hbar \gamma_{\mathrm{I}} \boldsymbol{I} \cdot (\mathbf{1} - \boldsymbol{\sigma}) \cdot \boldsymbol{H}_0 \\ = -\hbar \gamma_{\mathrm{I}} \sum_{pq} (\delta_{pq} - \sigma_{pq})\, H_{0q} I_p\,, \\ (p, q = 1, 2, 3 \equiv x, y, z),\end{aligned} \tag{1}$$

where σ_{pq} is the chemical shift tensor (screening tensor), δ_{pq} is Kronecker's delta, I_p are components of nuclear spin, $H_{0q} = H_0\, \delta_{pq}$ are the components of the field H_0 in the laboratory frame, and γ_{I} 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:

$$G = \sum_{pq} T_{pq} A_{qp}\,, \tag{2}$$

$$T_{pq} = (\sigma_{pq} - \delta_{pq})\, \omega_0 \equiv (\sigma_{pq} - \delta_{pq})\, \gamma_{\mathrm{I}} H_0\,, \tag{3}$$

$$A_{qp} = n_{0q} I_p \equiv (H_{0q}/H_0)\, I_p\,, \tag{4}$$

where ω_0 is the Larmor precession angular frequency and $\boldsymbol{n}_0$ is a unit vector along the $\boldsymbol{H}_0$ field.

The tensors T_{pq} and A_{qp} may be reduced into the irreducible spherical tensors F_{lm} and tensor operators $A_{lm}(\boldsymbol{I}, \boldsymbol{n}_0)$ 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:

$$G = \sum_{l=0}^{2} G^{(l)} = \sum_{l=0}^{2} \sum_{m=-l}^{l} (-1)^m A_{lm}(\boldsymbol{I}, \boldsymbol{n}_0)\, F_{l-m}\,, \tag{5}$$

where in the laboratory frame one gets

$$A_{00}(\boldsymbol{I}, \boldsymbol{n}_0) = \boldsymbol{I} \cdot \boldsymbol{n}_0 = I_z\,, \tag{6}$$

$$A_{10}(\boldsymbol{I}, \boldsymbol{n}_0) = -\tfrac{1}{2} (I_+ n_- - I_- n_+) = 0\,, \tag{7}$$

$$A_{1\pm1}(\boldsymbol{I}, \boldsymbol{n}_0) = -\frac{1}{\sqrt{2}} (I_\pm n_z - I_z n_\pm) = -\frac{1}{\sqrt{2}} I_\pm\,, \tag{8}$$

$$A_{20}(\boldsymbol{I}, \boldsymbol{n}_0) = I_z n_z - \tfrac{1}{4} (I_+ n_- + I_- n_+) = I_z\,, \tag{9}$$

$$A_{2\pm1}(\boldsymbol{I}, \boldsymbol{n}_0) = \mp \frac{\sqrt{6}}{4} (I_z n_\pm + I_\pm I_z) = \mp \frac{\sqrt{6}}{4} I_\pm\,, \tag{10}$$

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$$A_{2\pm 2}(\boldsymbol{I}, \boldsymbol{n}_0) = \frac{\sqrt{6}}{4} I_\pm n_\pm \equiv \frac{\sqrt{6}}{4} \cdot (I_x \pm i I_y)(n_x \pm i n_y) = 0, \quad (11)$$

$$F_{00} = \tfrac{1}{3} \sum_p T_{pp} \equiv -\omega_0 (1-\sigma), \quad (12)$$

$$F_{10} = -\frac{i\,\omega_0}{2} (\sigma_{xy} - \sigma_{yx}), \quad (13)$$

$$F_{1\pm 1} = \frac{\omega_0}{2\sqrt{2}} [(\sigma_{xz} - \sigma_{zx}) \pm i(\sigma_{yz} - \sigma_{zy})], \quad (14)$$

$$F_{20} = \omega_0 (\sigma_{zz} - \sigma), \quad (15)$$

$$F_{2\pm 1} = \mp \frac{\omega_0}{\sqrt{6}} [(\sigma_{xz} + \sigma_{zx}) \pm i(\sigma_{yz} + \sigma_{zy})], \quad (16)$$

$$F_{2\pm 2} = \frac{\omega_0}{\sqrt{6}} [\sigma_{xx} - \sigma_{yy} \pm i(\sigma_{xy} + \sigma_{yx})], \quad (17)$$

where $\sigma = \frac{1}{3} \mathrm{Tr}\, \boldsymbol{\sigma}$ 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. Moreover, in the case of spins exchanging positions between two sites with chemical shifts $+\delta\omega/2$ and $-\delta\omega/2$ from ω_0, also the term $G^{(0)}$ can provide a relaxation mechanism [16]. 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 τ_{cl} for the interactions $G^{(l)}$ 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 $2H_1 \cos\omega t$ 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 $T_{1\varrho}$ and $T_{2\varrho}$ in the RF:

$$\frac{1}{T_{N\varrho}} = \sum_{l=0}^{2} \frac{1}{T_{N\varrho}^{(l)}} = \sum_{l=0}^{2} \sum_{m,m'=-l}^{l} 12\, c_l \begin{pmatrix} 1 & 1 & 1 \\ m'-N+1 & N-1 & -m' \end{pmatrix}^2 \begin{pmatrix} 1 & 1 & l \\ m & 0 & -m \end{pmatrix}^2 (d^{(1)}_{mm'}(\beta))^2 \frac{\tau_{cl}}{1+(m\,\omega + m'\,\omega_e)^2 \tau_{cl}^2}, \quad (N=1,2), \quad (18)$$

where

$$c_0 = \tfrac{3}{8} (\delta\omega)^2, \quad (19)$$

$$c_1 = \tfrac{1}{4} \omega_0^2 (\delta\sigma)^2 \equiv \tfrac{1}{4} \omega_0^2 [(\sigma_{xy} - \sigma_{yx})^2 + (\sigma_{xz} - \sigma_{zx})^2 + (\sigma_{yz} - \sigma_{zy})^2], \quad (20)$$

$$c_2 = \tfrac{1}{3} \omega_0^2 (\Delta\sigma)^2 \equiv \tfrac{1}{3} \omega_0^2 \{ (\sigma_{zz} - \sigma_{xx})(\sigma_{zz} - \sigma_{yy}) + (\sigma_{xx} - \sigma_{yy})^2 + \tfrac{3}{4} [(\sigma_{xy} + \sigma_{yx})^2 + (\sigma_{xz} + \sigma)^2 + (\sigma_{yz} + \sigma_{zy})^2] \}, \quad (21)$$

$$\omega_e = \gamma_I H_e = \sqrt{(\omega_0 - \omega)^2 + \omega_1^2}, \quad (22)$$

$$\omega_1 = \gamma_I H_1, \quad (23)$$

$$\beta = \mathrm{arc\,tg}[\omega_1/(\omega_0 - \omega)], \quad (24)$$

where $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are Wigner's $3j$ symbols [13–15], $d^{(l)}_{mm'}(\beta)$ is the transformation matrix for rotation around y-axis through the angle β between the direction of H_0 field and the effective field H_e in the RF [11, 15], $\delta\sigma$ and $\Delta\sigma$ are the asymmetry and anisotropy parameters for the screening tensor σ_{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

$$\left(\frac{1}{T_{N\varrho}} \right)_{\omega_e = \beta = 0} = \frac{1}{T_N}, \quad (N=1,2), \quad (25)$$

where $d^{(l)}_{mm'}(0) = \delta_{mm'}$.

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 [2, 3] and the expression for $T_{1\varrho}$ in the presence of spin exchange for chair-to-chair isomerization [16], where $\tau_{c0} = \tau_e$. 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 $T_{1\varrho}$ and $T_{2\varrho}$ due to the symmetric and antisymmetric part of the chemical shift anisotropy. In the case of isotropic molecular reorientations, when $\tau_{c1}/3 = \tau_{c2} \equiv \tau_c$ and under normal resonance conditions ($\omega = \omega_0$, $\beta = \pi/2$, $\omega_1 \ll \omega_0$) it follows that:

$$\frac{1}{T_{1\varrho}} = \frac{(\delta\omega)^2}{4} \frac{\tau_e}{1+\omega_1^2 \tau_e^2} + \frac{\omega_0^2 (\delta\sigma)^2}{4} \frac{\tau_e}{1+9\,\omega_0^2 \tau_e^2} + \frac{\omega_0^2 (\varDelta\sigma)^2}{45} \tau_c \left(\frac{4}{1+\omega_1^2 \tau_c^2} + \frac{3}{1+\omega_0^2 \tau_c^2} \right), \tag{26}$$

$$\frac{1}{T_{2\varrho}} = \frac{(\delta\omega)^2}{8} \frac{\tau_c}{1+\omega_1^2 \tau_c^2} + \frac{3\,\omega_0^2 (\delta\sigma)^2}{8} \frac{\tau_c}{1+9\,\omega_0^2 \tau_c^2} + \frac{\omega_0^2 (\varDelta\sigma)^2}{90} \tau_c \left(\frac{4}{1+\omega_1^2 \tau_c^2} + \frac{9}{1+\omega_0^2 \tau_c^2} \right). \tag{27}$$

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

$$\frac{1}{T_1} = \frac{\omega_0^2 (\delta\sigma)^2}{2} \frac{\tau_c}{1+9\,\omega_0^2 \tau_c^2} + \frac{2\,\omega_0^2 (\varDelta\sigma)^2}{15} \frac{\tau_c}{1+\omega_0^2 \tau_c^2}, \tag{28}$$

$$\frac{1}{T_2} = \frac{(\delta\omega)^2}{4} \tau_e + \frac{\omega_0^2 (\delta\sigma)^2}{4} \frac{\tau_c}{1+9\,\omega_0^2 \tau_c^2} + \frac{\omega_0^2 (\varDelta\sigma)^2}{45} \tau_c \left(4 + \frac{3}{1+\omega_0^2 \tau_c^2} \right). \tag{29}$$

One can note that for sufficiently low field H_1 one gets $T_{1\varrho} = T_2$. In the extreme narrowing case it follows from Eqs. (26) – (29) that $T_1 \neq T_2$ and $T_{1\varrho} \neq T_{2\varrho}$ and under appropriate conditions it may be even possible to find $T_1 < T_2$ if $(\delta\sigma)^2 > \frac{4}{45} (\varDelta\sigma)^2$ 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}F, ^{13}C and ^{31}P [4–7]. It seems that investigation of the field dependence of T_1, T_2, $T_{1\varrho}$ and $T_{2\varrho}$ may be a basis for discovery of the antisymmetric part of the screenning tensors which is unobservable in NMR spectra.

In the considerations presented we have neglected relaxation contribtions 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.

Acknowledgements

The author wishes to thank Professor J. S. WAUGH, Dr. U. HAEBERLEN and Dr. H. W. SPIESS for helpful discussions.

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