Nuclear Magnetic Relaxation by Anisotropic Spin-Spin Interaction

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Nuclear relaxation times T_1, T_2, $T_{1\varrho}$, and $T_{2\varrho}$ are calculated in the weak collision limit for the case of anisotropic spin-spin interaction which includes dipole-dipole coupling and electron-coupled interactions in their most general form.

Introduction

The problem of nuclear relaxation through spin-spin interactions has been considered in many papers $^{1-12}$, special interest being devoted to dipolar and scalar relaxation, both in the laboratory frame (l. c. $^{1-5}$), and in the rotating frame $^{6-12}$. The purpose of this paper is to calculate the relaxation rates in the presence of a more general anisotropic spin-spin interaction employing a weak-collision approach.

Theory

Consider a system of nuclear spins in the presence of strong static Zeeman interaction and spin-spin interaction which can be treated as a random time dependent small perturbation. The spin-spin interaction is composed of diret dipole-lipide coupling $\boldsymbol{D}$ and indirect interaction via the electrons, $\boldsymbol{J}$. The appropriate Hamiltonian for the interaction of nuclear spins I and S is

$$\mathcal{H} \equiv \hbar\, G = \hbar\, I \cdot (\boldsymbol{D} + \boldsymbol{J}) \cdot S = \hbar \sum_{pq} (D_{pq} + J_{pq})\, I_p\, S_q \,, \tag{1}$$

$$D_{pq} = \hbar\, \gamma_I\, \gamma_S\, r^{-3} (\delta_{pq} - 3\, n_p\, n_q)\,, \quad (pq = 1, 2, 3 \equiv x, y, z)\,, \tag{2}$$

where γ_I and γ_S are gyromagnetic ratios, δ_{pq} is Kronecker's delta and n_p, n_q and r are the direction cosines of the internuclear vector $\boldsymbol{r}$ and its length, respectively. D_{pq} is symmetric and traceless with five independent components whereas the tensor J_{pq} is not necessarily symmetric and in general has nine independent components and a non-vanishing trace. The indirect spin-spin interaction tensor J_{pq} can be written as the sum of our terms: an orbital term, a spin dipolar term, a Fermi contact term and a Fermi-spin dipolar cross term $^{13, 14}$. The first two terms are unsymmetric. The third one is isotropic and diagonal, and the last one is symmetric and traceless. The resulting tensor J_{pq} is then unsymmetric. One can easily note that the Hamiltonian (1) may be written as a contraction of two cartesian tensors of the second order, namely:

$$G = \sum_{pq} T_{pq}\, A_{qp}\,, \tag{3}$$

$$T_{pq} = D_{pq} + J_{pq}\,, \tag{4}$$

$$A_{qp} = I_p\, S_q\,. \tag{5}$$

The cartesian tensors T_{pq} and A_{qp}, which generally have nine components, may be reduced into the spherical tensors F_{lm} and tensor operators $A_{lm}(I, S)$ of orders $l = 0, 1, 2$, respectively $^{15-17}$ and the Hamiltonian (1) may be written in the form:

$$G = \sum_{l=0}^{2} G^{(l)} = \sum_{l=0}^{2} \sum_{m=-l}^{l} (-1)^m A_{lm}(I, S)\, F_{l-m}\,, \tag{6}$$

where

$$A_{00}(I, S) = I \cdot S\,, \tag{7}$$

$$A_{10}(I, S) = -\tfrac{1}{2}\,(I_+ S_- - I_- S_+)\,, \tag{8}$$

$$A_{1\pm1}(I, S) = -\frac{1}{\sqrt{2}}\,(I_\pm S_z - I_z S_\pm)\,, \tag{9}$$

$$A_{20}(I, S) = I_z S_z - \tfrac{1}{4}\,(I_+ S_- + I_- S_+)\,, \tag{10}$$

$$A_{2\pm1}(I, S) = \mp \frac{\sqrt{6}}{4}\,(I_z S_\pm + I_\pm S_z)\,, \tag{11}$$

$$A_{2\pm2}(I, S) = \frac{\sqrt{6}}{4}\, I_\pm\, S_\pm \equiv \frac{\sqrt{6}}{4}\,(I_x \pm i\, I_y)\,(S_x \pm i\, S_y)\,, \tag{12}$$

$$F_{00} = \tfrac{1}{3} \sum_p J_{pp} \equiv J\,, \tag{13}$$

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$$F_{10} = -\frac{i}{2}(J_{xy} - J_{yx}), \tag{14}$$

$$F_{1\pm1} = \frac{1}{2\sqrt{2}}[(J_{xz} - J_{zx}) \pm i(J_{yz} - J_{zy})], \tag{15}$$

$$F_{20} = T_{zz} - J = \tfrac{1}{3}(2T_{zz} - T_{xx} - T_{yy}), \tag{16}$$

$$F_{2\pm1} = \mp\frac{1}{\sqrt{6}}[(T_{xz} + T_{zx}) \pm i(T_{yz} + T_{zy})], \tag{17}$$

$$F_{2\pm2} = \frac{1}{\sqrt{6}}[T_{xx} - T_{yy} \pm i(T_{xy} + T_{yx})]. \tag{18}$$

According to the above equations the resulting spin-spin interaction can be decomposed into indirect scalar interaction ($l=0$), an indirect anisotropic-antisymmetric interaction ($l=1$) and an anisotropic-symmetric interaction ($l=2$), where the last one contains both dipolar and indirect coupling contributions.

In the presence of spin exchange and molecular motion the spherical tensors F_{lm} may be treated as random functions of time and the time dependent spin-spin interaction gives contributions to the relaxation rate. The indirect scalar interaction can contribute to the relaxation only in the case of unlike spins [3], whereas the anisotropic interactions can contribute both in the case of like and unlike spins.

As a first example we consider a system of like spins ($I=S$, $\gamma_I=\gamma_S$) in the presence of an external magnetic field H_0 along the z-axis and a radiofrequency field $2H_1\cos\omega t$ along the x-axis of the laboratory frame. Using the method presented elsewhere [12] and taking into account well known transformation properties and commutation relations for spherical tensors and tensor operators respectively (l. c. [15–17]) one can find the following expression for the relaxation times $T_{1\varrho}$ and $T_{2\varrho}$ in the rotating frame

$$\frac{1}{T_{N\varrho}} = \sum_{l=1}^{2} \sum_{m,m'=-l}^{l} c_l\, l(l+1)(2l+1)\, I(I+1) \cdot \begin{pmatrix} l & 1 & l \\ m'-N+1 & N-1 & -m' \end{pmatrix}^2 (d_{mm'}^{(l)}(\beta))^2 \cdot \frac{\tau_{cl}}{1+(m\,\omega+m'\,\omega_e)^2\,\tau_{cl}^2}, \quad (N=1,2), \tag{19}$$

$$c_1 = \tfrac{1}{12}(\delta J)^2 \equiv \tfrac{1}{12}[(J_{xy}-J_{yx})^2 + (J_{xz}-J_{zx})^2 + (J_{yz}-J_{zy})^2], \tag{20}$$

$$c_2 = \tfrac{1}{9}(\varDelta T)^2 \equiv \tfrac{1}{9}\{(T_{zz}-T_{xx})(T_{zz}-T_{yy}) + (T_{xx}-T_{yy})^2 + \tfrac{3}{4}[(T_{xy}+T_{yx})^2 + (T_{xz}+T_{zx})^2 + (T_{yz}+T_{zy})^2]\}, \tag{21}$$

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

$$\omega_0 = \gamma_I H_0, \quad \omega_1 = \gamma_I H_1, \tag{23}$$

$$\beta = \operatorname{arctg}[\omega_1/(\omega_0-\omega)], \tag{24}$$

where $\begin{pmatrix} I_1 & I_2 & I_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ are Wigner's $3j$ symbols [15–17], δJ and $\varDelta T$ the asymmetry and anisotropy parameters for the tensors J_{pq} and T_{pq} in the molecular reference frame respectively, $d_{mm'}^{(l)}(\beta)$ the transformation matrix for the rotation around the y-axis through the angle β between the directions of the H_0 field and the effective field H_e in the rotating frame [12, 17] and τ_{cl} are the correlation times for the interactions $G^{(l)}$. In the case of isotropic molecular motion which is assumed in the presented calculations, one can take

$$\tfrac{1}{3}\tau_{c1} = \tau_{c2} \equiv \tau_c\,. \tag{25}$$

In the case of unlike spins I and S, where I are resonant ones, the following relations for $T_{1\varrho}$ and $T_{2\varrho}$ can be obtained similarly:

$$\frac{1}{T_{N\varrho}} = \sum_{l=0}^{2} \sum_{m\,m_1 m_2 m_1'} 12\,c_l\,S(S+1) \cdot \begin{pmatrix} 1 & 1 & 1 \\ m_1'-N+1 & N-1 & -m_1' \end{pmatrix}^2 \begin{pmatrix} 1 & 1 & l \\ m_1 & m_2 & -m \end{pmatrix}^2 \cdot (d_{m_1 m_1'}^{(1)}(\beta))^2\, \frac{\tau_{cl}}{1+(m_1\,\omega+m_2\,\omega_S+m_1'\,\omega_e)^2\,\tau_{cl}^2}, \tag{26}$$

where $c_0 = J^2/2$.

From Eqs. (19) and (24) one can easily get expressions for the relaxation times T_1 and T_2 in the laboratory frame, namely:

$$\left(\frac{1}{T_{N\varrho}}\right)_{\omega_e=\beta=0} = \frac{1}{T_N}, \quad (N=1,2), \tag{27}$$

where ohne should note that $d_{mm'}^{(l)}(0) = \delta_{mm'}$.

From the above general formulas for the relaxation times one can obtain known expressions for T_1, T_2, $T_{1\varrho}$ and $T_{2\varrho}$ in the case of pure dipolar or scalar relaxation [8–12] as well as the relaxation contributions due to the anisotropic spin-spin interaction.

As a special case we consider the relaxation for a system of like spins at normal resonance conditions ($\omega=\omega_0$, $\omega_1 \ll \omega_0$). In this case from Eqs. (19) to (25) it follows that

$$\frac{1}{T_{1\varrho}} = \frac{(\delta J)^2}{12} I(I+1)\,\tau_c \left(\frac{1}{1+9\,\omega_1^2\,\tau_c^2} + \frac{1}{1+9\,\omega_0^2\,\tau_c^2}\right) + \frac{(\varDelta T)^2}{45} I(I+1)\,\tau_c \cdot \left(\frac{3}{1+\omega_1^2\,\tau_c^2} + \frac{5}{1+\omega_1^2\,\tau_c^2} + \frac{2}{1+\omega_0^2\,\tau_c^2}\right), \tag{28}$$

$$\frac{1}{T_{2Q}} = \frac{(\delta J)^2}{24} I(I+1)\,\tau_c \left(\frac{1}{1+4\,\omega_0^2\,\tau_c^2} + \frac{3}{1+9\,\omega_1^2\,\tau_c^2}\right) + \frac{(\Delta T)^2}{180} I(I+1)\,\tau_c \cdot \left(3 + \frac{3}{1+9\,\omega_0^2\,\tau_c^2} + \frac{14}{1+4\,\omega_1^2\,\tau_c^2} + \frac{20}{1+\omega_0^2\,\tau_c^2}\right). \tag{29}$$

Moreover, using Eq. (27) one can get

$$\frac{1}{T_1} = \frac{(\delta J)^2}{6} I(I+1) \frac{\tau_c}{1+9\,\omega_0^2\,\tau_c^2} + \frac{2(\Delta T)^2}{45} I(I+1)\,\tau_c \left(\frac{1}{1+\omega_0^2\,\tau_c^2} + \frac{4}{1+4\,\omega_0^2\,\tau_c^2}\right), \tag{30}$$

$$\frac{1}{T_2} = \frac{(\delta J)^2}{12} I(I+1)\,\tau_c \left(1 + \frac{1}{1+9\,\omega_0^2\,\tau_c^2}\right) + \frac{(\Delta T)^2}{45} I(I+1)\,\tau_c \left(3 + \frac{5}{1+\omega_0^2\,\tau_c^2} + \frac{2}{1+4\,\omega_0^2\,\tau_c^2}\right). \tag{31}$$

If there is axial symmetry of the tensor J_{pq} around the internuclear axis then in the molecular frame the J_{pq} has only two independent components $J_{zz} = J_{\|}$ and $J_{xx} = J_{yy} = J_{\perp}$, whereas $\delta J = 0$. In such a special case one should insert into the previous relations the following value of ΔT:

$$\Delta T = \Delta J - 3\,d = -3\,d(1 - \tfrac{1}{3}\varkappa), \tag{32}$$

where

$$\Delta J = J_{\|} - J_{\perp}, \quad d = \hbar\,\gamma_I\,\gamma_S\,r^{-3}, \quad \varkappa = \Delta J/d. \tag{33}$$

Discussion

By comparing the above expressions for the relaxation times with those for dipolar contribution $(T_{N_Q})_{\text{dip}}$ [8, 12] one can see that in the presence of indirect spin-spin interaction in a linear molecule the effective relaxation rate may be expressed in the form

$$\frac{1}{T_{N_Q}} = \left(\frac{1}{T_{N_Q}}\right)_{\text{dip}} (1 - \tfrac{1}{3}\varkappa)^2. \tag{34}$$

The factor which appears in Eq. (34) may be important in the case of heavy nuclei, where $\varkappa$ is sufficiently big, e. g. using the experimental data for the *TlF* molecule one can find $\varkappa = 1.54 \pm 0.11$ [13, 18] and hence $(1 - \frac{1}{3}\varkappa)^2 = 0.237 \pm 0.036$. This means that the intramolecular relaxation contributions due to the resultant spin-spin interaction in *TlF* should be more than four times smaller than that following from dipole-dipole interaction itself. This is an example of interference between dipolar interaction and indirect spin-spin interaction in the nuclear magnetic relaxation process. These interference effects must be taken into account in the case of relaxation of heavy nuclei.

Moreover, in the case of nonlinear molecules the antisymmetric part of the spin-spin interaction should be taken into account. Unfortunately, except some theoretical calculations [14], nothing is known experimentally about the size of this contribution, but it well may be important for heavy atoms in unsymmetrical molecular environments.

One should also note that the antisymmetric part of the screening tensor, unobservable in NMR spectra [19], can be an additional source of the relaxation. This effect will be considered elsewhere.

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