

Title	Nuclear Magnetic Spin-Rotational Relaxation Times for Symmetric Molecules
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Date	1981
Citation	McConnell, James (1981) Nuclear Magnetic Spin-Rotational Relaxation Times for Symmetric Molecules. (Preprint)
URL	https://dair.dias.ie/id/eprint/945/
DOI	DIAS-STP-81-22

NUCLEAR MAGNETIC SPIN-ROTATIONAL
RELAXATION TIMES FOR SYMMETRIC MOLECULES

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It is shown that the problem of calculating times related to nuclear magnetic spin-rotational interactions may be solved for the symmetric rotator model of a molecule by employing the method already proposed in a general manner for asymmetric molecules that undergo rotational thermal motion. Expressions are derived for the spin-rotational correlation time and for the contributions arising from spin-rotational interactions to the longitudinal and transverse relaxation times.

1. INTRODUCTION

A general analytical method of calculating nuclear magnetic relaxation times resulting from spin-rotational interactions has been based on the stochastic rotation operator and on the solution of stochastic differential equations¹⁾. The method is applicable in principle to molecules with no special symmetry which are subject to rotational thermal motion, but a thorough examination of this problem is hampered by the relatively low order of approximation to which calculations on the rotational Brownian motion of asymmetric bodies have so far been taken²⁾. The problem has already been solved for spherical molecules^{1,3,4,5)}. In the present paper the case of symmetric top molecules is examined. The results are true for a molecule which has a principal axis of inertia through the centre of mass that passes through the nucleus in which we are interested, and such that this principal axis is an axis of symmetry C_n for the molecule with $n \geq 3$ ⁶⁾.

2. GENERAL EQUATIONS

We consider nuclei in a rotating molecule denoting by \underline{I}_i the spin operator of the i th nucleus and by $\hbar \underline{J}_i$ the angular momentum of the molecule³⁾. The spin-rotational Hamiltonian of the i th nucleus

$$\hbar G_i = \hbar \underline{I}_i \cdot \underline{C}_i \cdot \underline{J}_i, \quad (1)$$

where \underline{C}_i is a dyadic. If $C_{\mu\nu}^i$ with $\mu, \nu = 1, 2, 3$ are the cartesian components of \underline{C}_i in the molecular frame of coordinates, which is taken in the directions of the principal axes of inertia through the centre of mass, we write

$$b_{\alpha\nu}^i = C_{3\nu}^i, \quad b_{\pm 1, \nu}^i = \mp \frac{C_{1\nu}^i \mp i C_{2\nu}^i}{\sqrt{2}}. \quad (2)$$

Then (1) is expressible as

$$G_i = \sum_{k=-1}^1 V_i^k U_i^k,$$

where V_i^k are the spherical components of \underline{I}_i in the laboratory system and

$$U_i^k = \sum_{\nu=1}^3 \sum_{m=-1}^1 b_{m\nu}^i D_{km}^i(\alpha_i, \beta_i, \gamma_i) J_{i\nu},$$

D_{km}^i being the rotation matrix for the transformation of a spherical tensor and $\alpha_i, \beta_i, \gamma_i$ the Euler angles specifying the molecular system with reference to the laboratory system of coordinates.

To introduce the various relaxation times we define $C_{ii}^{lk}(t)$ by

$$C_{ii}^{lk}(t) = \langle U_i^l(t) U_i^k(0) \rangle,$$

where the angular brackets denote ensemble average for thermal equilibrium. The Laplace transform $C_{ii}^{lk}(s)$ of $C_{ii}^{lk}(t)$ is expressible by⁷⁾

$$C_{ii}^{lk}(s) = \frac{1}{3\hbar^2} \sum_{\mu, \nu=1}^3 \sum_{m, n=-1}^1 (-1)^m b_{n\mu}^i b_{m\nu}^i I_\mu I_\nu \left(\int_0^\infty e^{-st} \langle R(t) \omega_\mu(t) \omega_\nu(0) \rangle dt \right)_{n,-m}. \quad (3)$$

In this I_μ, I_ν are the moments of inertia about the molecular μ - and ν - axes, and $\omega_\mu(t), \omega_\nu(0)$ the corresponding components of angular velocity of the molecule at times t and zero, respectively. $R(t)$ is the rotation operator that brings the molecular frame at time zero to its orientation at time t . The subscripts $n, -m$ signify the $n, -m$ matrix element with respect to the basis $Y_{2,-1}(\beta(0), \alpha(0)), Y_{2,0}(\beta(0), \alpha(0)), Y_{2,1}(\beta(0), \alpha(0))$, the $\alpha(0), \beta(0)$ being two of the above mentioned Euler angles at time zero.

The contributions $(1/T_1)_i, (1/T_2)_i$ from the spin-rotational interactions to the reciprocals $1/T_1, 1/T_2$ of the longitudinal and transverse relaxation times are given by

$$\left(\frac{1}{T_1}\right)_i = 2 J_i(\omega_0), \quad \left(\frac{1}{T_2}\right)_i = J_i(0) + J_i(\omega_0), \quad (4)$$

where ω_0 is the angular velocity of the Larmor precession and

$$J_i(\omega) = \frac{1}{2} \left(C_{ii}^{lk}(-i\omega) + C_{ii}^{lk}(i\omega) \right). \quad (5)$$

3. CALCULATION OF C_{10}^{00}

In the representation employed in eq. (3) we have

$$J_1 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, J_2 = \frac{i}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, J_3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad (12)$$

which clearly satisfy (10). From (12) we deduce that

$$J_1^2 = \begin{bmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, J_2^2 = \begin{bmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ 0 & 1 & 0 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{bmatrix}, J_3^2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$J_2 J_3 = \begin{bmatrix} 0 & 0 & 0 \\ -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & 0 & 0 \end{bmatrix}, J_3 J_2 = \begin{bmatrix} 0 & -\frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \\ 0 & \frac{i}{\sqrt{2}} & 0 \end{bmatrix}, J_1 J_2 = \begin{bmatrix} \frac{i}{2} & 0 & 0 \\ 0 & 0 & 0 \\ \frac{i}{2} & 0 & 0 \end{bmatrix}$$

$$J_2 J_1 = \begin{bmatrix} 0 & 0 & 0 \\ \frac{i}{2} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, J_3 J_1 = \begin{bmatrix} \frac{i}{2} & 0 & 0 \\ 0 & 0 & 0 \\ \frac{i}{2} & 0 & 0 \end{bmatrix} \quad (13)$$

and we verify that

$$J_1^2 + J_2^2 + J_3^2 = 2I.$$

We take the axis of symmetry of the molecule to be the third coordinate axis and then

$$T_2 = I, \quad B_2 = B, \quad D_2 = D, \quad (14)$$

so that from (9) and (13)

$$-G + aI = \begin{bmatrix} D_1 + D_3 + a & 0 & 0 \\ 0 & 2D_1 + a & 0 \\ 0 & 0 & D_1 + D_3 + a \end{bmatrix},$$

$$(-G + aI)^{-1} = \begin{bmatrix} (D_1 + D_3 + a)^{-1} & 0 & 0 \\ 0 & (2D_1 + a)^{-1} & 0 \\ 0 & 0 & (D_1 + D_3 + a)^{-1} \end{bmatrix}, \quad (15)$$

which is a diagonal matrix but in general not just a multiple of the identity matrix.

We now proceed to find C_{10}^{00} from (3) and (8), employing the results (12) - (15). In subsection 4.4 of ref. 1 it was found that the $J_\mu J_\nu$ -terms of (8) gave rise to calculational difficulties, so let us consider these first of all. From (3)

$$C_{10}^{00} = \frac{1}{3R^2} \sum_{\mu, \nu=1}^3 I_\mu I_\nu \sum_{m, n=-1}^1 (-1)^m R_{\mu\nu}^i R_{m\nu}^i \left(\int_0^\infty \langle R(t) R_0(t) \omega_\nu(t) \rangle dt \right)_{m, n=-m}. \quad (16)$$

We take the 9 different combinations of μ, ν separately and perform the summations over m and n for the $J_\mu J_\nu$ -terms of (8). Let us, for example, take $\mu=2, \nu=3$: This gives a contribution

$$-\frac{(2T)^2}{3R^2 B_1 B_2} \sum_{m, n=-1}^1 (-1)^m R_{2,2}^i R_{3,3}^i J_2 J_3 [(-G)^{-1} - (-G + B_1 I)^{-1}] \\ = (-G + B_2 I)^{-1} + (-G + [B_2 + B_3] I)^{-1}. \quad (17)$$

Since the third axis is the axis of symmetry, the components of the dyadic C^i in the molecular frame satisfy¹⁰⁾

$$C_{33}^i = C_{11}^i, \quad C_{11}^i = C_{22}^i = C_{\perp}^i$$

$$C_{p\nu}^i = 0. \quad (p \neq \nu)$$

We then deduce from (2) that

$$b_{\pm 1,1}^i = \mp \frac{C_{\perp}^i}{\sqrt{2}}, \quad b_{\pm 1,2}^i = \frac{i C_{\perp}^i}{\sqrt{2}}, \quad b_{\pm 1,3}^i = 0 \quad (18)$$

$$b_{01}^i = b_{02}^i = 0, \quad b_{03}^i = C_{11}^i.$$

Let us consider

$$\sum_{m,n=-1}^1 (-)^m b_{m2}^i b_{m3}^i \left(J_2 J_3 (-G + a \underline{I})^{-1} \right)_{n,-m} \quad (19)$$

Since, by (13) and (15),

$$J_2 J_3 (-G + a \underline{I})^{-1} = -\frac{i}{\sqrt{2}} \begin{bmatrix} 0 & 0 & 0 \\ (D_1 + D_3 + a)^{-1} & 0 & (D_1 + D_3 + a)^{-1} \\ 0 & 0 & 0 \end{bmatrix},$$

the sum (19) is equal to

$$-\frac{i (b_{02}^i b_{02}^i + b_{02}^i b_{03}^i)}{\sqrt{2} (D_1 + D_3 + a)},$$

which vanishes by (18). Taking a successively equal to $0, B_1, B_3, B_1 + B_3$

we deduce that (17) vanishes. It may similarly be shown for all

combinations of μ and ν that

$$\sum_{m,n=-1}^1 (-)^m b_{m\mu}^i b_{m\nu}^i \left(J_{\mu} J_{\nu} (-G + a \underline{I})^{-1} \right)_{n,-m} = 0 \quad (20)$$

Then by putting a successively equal to $0, B_1, B_3, B_1 + B_3$ we conclude

from (20) that the $J_{\mu} J_{\nu}$ -term of (8) gives no contribution to $C_{ii}^{(0)}$

even before the summation over μ, ν is carried out.

The contribution to $C_{ii}^{(0)}$ from the first term on the right hand

side of (8),

$$\frac{kT}{3\mathcal{L}^2} \sum_{\mu=1}^3 I_{\mu} \sum_{m,n=-1}^1 (-)^m b_{n\mu}^i b_{m\mu}^i \left[\begin{matrix} (D_1 + D_3 + B_{\mu})^{-1} & 0 & 0 \\ 0 & (2D_1 + B_{\mu})^{-1} & 0 \\ 0 & 0 & (D_1 + D_3 + B_{\mu})^{-1} \end{matrix} \right]_{n,-m}$$

$$= \frac{kT}{3\mathcal{L}^2} \sum_{\mu=1}^3 I_{\mu} \left\{ -(b_{-1\mu}^i b_{1\mu}^i + b_{2\mu}^i b_{-1\mu}^i) (D_1 + D_3 + B_{\mu})^{-1} + b_{0\mu}^i b_{0\mu}^i (2D_1 + B_{\mu})^{-1} \right\}$$

$$= \frac{kT}{3\mathcal{L}^2} \left\{ \frac{2I_1 C_{\perp}^2}{D_1 + D_3 + B_1} + \frac{I_3 C_{11}^2}{2D_1 + B_3} \right\}, \quad (21)$$

by (18).

The other terms in (8) that give a contribution to $C_{ii}^{(0)}$ are proportional to $(kT)^2$ and they include no term proportional to $(-G + a \underline{I})^{-1}$. Moreover they are correct only to order $(kT)^2 / (I^2 B^3)$, where for the moment we suppress the suffixes of I and B . We may therefore replace $(-G + a \underline{I})^{-1}$ in them by $a^{-1} \underline{I}$.

Let us examine the contribution to $C_{ii}^{(0)}$ from

$$\sum_{\mu=1}^3 \frac{kT}{I_{\mu}} \sum_{i=1}^3 \gamma_i J_i^2 \left(\frac{1}{B_{\mu}} - \frac{1}{B_{\mu} + B_i} \right)$$

where $\gamma_i = kT / (I_i B_i)$. This contribution is from (13), (16) and (18)

$$\begin{aligned}
 & \frac{kT}{3k^2} \sum_{\mu=1}^3 \Gamma_{\mu} \left[\sum_{\nu=1}^3 \gamma_{\nu} \left(\frac{1}{B_{\mu}} - \frac{1}{B_{\mu} + B_{\nu}} \right) \sum_{m, n=1}^1 (-1)^m \rho_{m\nu}^i \rho_{n\mu}^i (\Gamma_{\nu}^2) \right. \\
 & \left. - \frac{kT}{3k^2} \sum_{\mu=1}^3 \left[\gamma_{\mu} \left(\frac{1}{B_{\mu}} - \frac{1}{B_{\mu} + B_{\mu}} \right) (-2 \rho_{\mu\mu}^i \rho_{\mu\mu}^i + 2 (\rho_{\mu\mu}^i)^2) \right. \right. \\
 & \left. \left. + \gamma_{\nu} \left(\frac{1}{B_{\mu}} - \frac{1}{B_{\mu} + B_{\nu}} \right) (-2 \rho_{\mu\nu}^i \rho_{\nu\mu}^i) \right] \right]
 \end{aligned}$$

$$= \frac{(kT)^2}{3k^2} \left\{ \frac{C_1^2}{B_1^3} + \frac{2I_1 C_1^2}{I_3 B_1 B_2 (B_1 + B_2)} + \frac{2I_3 C_1^2}{I_1 B_1 B_2 (B_1 + B_2)} \right\} \quad (22)$$

Similarly it is deduced that the last $\rho_{\mu\nu}^i$ -term in (8) gives a contribution

$$= \frac{2(kT)^2 C_1^2 (I_1 - I_3)^2}{3k^2 I_1 I_3 B_1^2 (B_1 + B_2)} \quad (23)$$

Of the two terms proportional to $(\sum_{\nu} \rho_{\mu\nu}^i \rho_{\nu\mu}^i)$ in (8) the first is approximated for $\rho \ll D$ by

$$= \frac{(kT)^2 (\sum_{\nu} \rho_{\mu\nu}^i \rho_{\nu\mu}^i)}{I_1^2 I_3 B_{\mu} B_{\nu}} \left[\frac{I_{\mu} - I_{\nu}}{B_{\mu} + B_{\nu}} + \frac{I_{\nu} - I_{\mu}}{B_{\nu} + B_{\mu}} \right],$$

and the contribution of this to $C_{\mu\nu}^i(0)$ is

$$= \frac{(kT)^2}{3k^2} \sum_{\mu, \nu=1}^3 \frac{I_{\mu} I_{\nu}}{B_{\mu} B_{\nu}} \left[\frac{I_{\mu} - I_{\nu}}{B_{\mu} + B_{\nu}} + \frac{I_{\nu} - I_{\mu}}{B_{\nu} + B_{\mu}} \right] \sum_{m, n=1}^1 (-1)^m \rho_{m\mu}^i \rho_{n\nu}^i (\sum_{\nu} \rho_{\mu\nu}^i \rho_{\nu\mu}^i)_{\mu, \nu=1} \quad (24)$$

For the sum of the combinations $\mu=2, \nu=3$ and $\mu=3, \nu=2$ this yields

$$= \frac{2(kT)^2 C_1 C_1 (I_1 - I_3)}{3k^2 I_1 B_1 B_2 (B_1 + B_2)} \quad (25)$$

Similarly for the combinations $\mu=3, \nu=1$ and $\mu=1, \nu=3$ gives

$$= \frac{2(kT)^2 C_1 C_1 (I_1 - I_3)}{3k^2 I_1 B_1 B_2 (B_1 + B_2)} \quad (26)$$

and for $\mu=1, \nu=2$ and $\mu=2, \nu=1$

$$= \frac{4(kT)^2 C_1^2 (I_1 - I_3)}{3k^2 I_3 B_1^2 (B_1 + B_2)} \quad (27)$$

On summing (25), (26) and (27) we obtain

$$\begin{aligned}
 & \frac{(kT)^2}{3k^2} \sum_{\mu, \nu=1}^3 \frac{I_{\mu} I_{\nu}}{B_{\mu} B_{\nu}} \left[\frac{I_{\mu} - I_{\nu}}{B_{\mu} + B_{\nu}} + \frac{I_{\nu} - I_{\mu}}{B_{\nu} + B_{\mu}} \right] \sum_{m, n=1}^1 (-1)^m \rho_{m\mu}^i \rho_{n\nu}^i (\sum_{\nu} \rho_{\mu\nu}^i \rho_{\nu\mu}^i) \\
 & = \frac{4(kT)^2 (I_1 - I_3)}{3k^2 B_1 (B_1 + B_2)} \left[\frac{C_1^2}{I_3 B_1} - \frac{C_1 C_1}{I_1 B_2} \right].
 \end{aligned} \quad (28)$$

Proceeding in the same way we find that the contribution of the remaining term in (8) to $C_{\mu\nu}^i(0)$ is given by

$$\begin{aligned}
 & = \frac{(kT)^2}{3k^2} \sum_{\mu, \nu=1}^3 \frac{1}{B_{\mu} B_{\nu} (B_{\mu} + B_{\nu})} \sum_{m, n=1}^1 (-1)^m \rho_{m\mu}^i \rho_{n\nu}^i (\sum_{\nu} \rho_{\mu\nu}^i \rho_{\nu\mu}^i)_{\mu, \nu=1} \\
 & = \frac{(kT)^2}{3k^2} \left\{ \frac{1}{B_1 B_2 (B_1 + B_2)} + \frac{C_1^2}{B_1^3} \right\}.
 \end{aligned} \quad (29)$$

On collecting our results from (21) - (23), (28), (29) we conclude that

$$C_{ii}^{\infty(0)} = \frac{kT}{3k^2} \left\{ \frac{2I_1 C_{\perp}^2}{B_1 + D_1 + D_3} + \frac{I_3 C_{\parallel}^2}{B_3 + 2D_1} \right. \\ \left. + kT \left[\left(\frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \right) C_{\perp}^2 \right. \right. \\ \left. \left. + \frac{2I_3 (C_{\parallel}^2 + 2C_{\perp} C_{\parallel})}{I_1 B_1 B_3 (B_1 + B_3)} \right] \right\}. \quad (30)$$

As a check on this result we examine what it reduces to when the symmetric molecule is spherical. We put

$$I_1 = I_3 = I, \quad B_1 = B_3 = B$$

$$D_1 = D_3 = D = \frac{kT}{IB}$$

by (11), and write $D/B = kT/(IB^2) = \gamma$. Then (30) becomes

$$C_{ii}^{\infty(0)} = \frac{kTI}{3k^2 B} \left\{ \frac{2C_{\perp}^2}{1+2\gamma} + \frac{C_{\parallel}^2}{1+2\gamma} + \gamma (3C_{\perp}^2 + C_{\parallel}^2 + 2C_{\perp} C_{\parallel}) \right\} \\ = \frac{kTI}{3k^2 B} \left\{ 2C_{\perp}^2 + C_{\parallel}^2 - \gamma (C_{\perp} - C_{\parallel})^2 \right\}.$$

We see from (6) that this agrees in the approximation of the present paper with the result of direct calculation¹¹⁾.

4. SPIN-ROTATIONAL CORRELATION TIMES

Equation (30) leads immediately to expressions for spin-rotational correlation times. For the extreme narrowing case we have from (6) that

$$\frac{1}{T_{sr}} = \frac{2kT}{3k^2} \left\{ \frac{2I_1 C_{\perp}^2}{B_1 + D_1 + D_3} + \frac{I_3 C_{\parallel}^2}{B_3 + 2D_1} \right. \\ \left. + kT \left[\left(\frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \right) C_{\perp}^2 \right. \right. \\ \left. \left. + \frac{2I_3 (C_{\parallel}^2 + 2C_{\perp} C_{\parallel})}{I_1 B_1 B_3 (B_1 + B_3)} \right] \right\}. \quad (31)$$

It is possible to generalize this result so as to find $(1/T_1)$, and $(1/T_2)$, from (4) and (5). We see from eq. (3) that in order to do this we would have to retain s when employing (8) for the evaluation of $C_{ii}^{\infty(s)}$. This would present no great difficulty but the calculations would be somewhat more complicated.

To find the spin-rotational correlation time from (7) we first deduce from (18) that

$$\sum_{\mu=1}^3 \sum_{m=-1}^1 (-1)^m b_{-m\mu}^i b_{m\mu}^i I_{\mu} \\ = I_1 (-2b_{11}^i b_{-11}^i - 2b_{12}^i b_{-12}^i) + I_3 (b_{03}^i)^2 \\ = 2I_1 C_{\perp}^2 + I_3 C_{\parallel}^2.$$

It then follows that

$$\tau_{s,i} = \frac{1}{2I_1 C_{\perp}^2 + I_3 C_{\parallel}^2} \left\{ \frac{2I_1 C_{\perp}^2}{B_1 + D_1 + D_3} + \frac{I_3 C_{\parallel}^2}{B_3 + 2D_1} \right. \\ \left. + kT \left[\left(\frac{2}{B_1^3} + \frac{2I_1}{I_3 B_1^2 B_3} - \frac{2I_3}{I_1 B_1^2 (B_1 + B_3)} \right) C_{\perp}^2 \right. \right. \\ \left. \left. + \frac{2I_3 (C_{\parallel}^2 + 2C_{\perp} C_{\parallel})}{I_1 B_1 B_3 (B_1 + B_3)} \right] \right\}.$$

5. CONCLUSION

The general method of finding the contributions to longitudinal and transverse relaxation times arising from spin-rotational interactions, which had been proposed for asymmetric molecules undergoing rotational Brownian motion, has been successfully applied to molecules with an axis of rotational symmetry. The calculations are possible because the terms in the Laplace transformation of $\langle R(t) \omega_x(t) \omega_y(0) \rangle$ that had caused difficulty for vanishing values of the parameter ζ , are found to give zero contributions. The spin-rotational correlation time has also been calculated.

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