

On the Role of Nuclear Spin Symmetry of Symmetric Top Molecules in Gas Phase Nuclear Magnetic Relaxation

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For symmetric top molecules the role of nuclear spin symmetry is included in the derivation of the nuclear magnetic relaxation rate. It is assumed that this is dominated by a spin-rotation mechanism. Of the three nuclear spin species which exist for ZX_2Y symmetric tops, it is found that the "zero frequency" $K = -1$ to $+1$ term results in two of the species relaxing with a different rate from the third. The difference, which allows a direct NMR evaluation of the relative values of $|C_{zz}|$ and $|C_{yy}|$, is enhanced at low temperatures.

On tient compte du rôle de la symétrie du spin nucléaire dans le calcul de relaxation magnétique nucléaire, pour des molécules ayant une configuration de toupie symétrique. On suppose que ce rôle est contrôlé par un mécanisme spin-rotation. Des trois types de spins nucléaires existant pour des toupies synétriques ZX_2Y , il appert que le terme de "fréquence nulle", $K = -1$ à $+1$, fait que deux de ces types ont un taux de relaxation différent de celui du troisième. Cette différence, qui permet une évaluation RMN directe de $|C_{zz}|$ et $|C_{yy}|$, est accrue aux basses températures. [Traduit par le journal]

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1. Introduction

Recently Armstrong and Courtney (1972) presented experimental data for the gas phase nuclear magnetic relaxation of several symmetric top molecules of the types ZX_2Y and ZX_3 . It was found by using the existing theories for the spin-rotation mechanism (Bloom, Bridges, and Hardy 1967, hereafter referred to as BBH; McCourt and Hess 1970, 1971) that the effective coupling constants C_{eff}^2 differed significantly from those obtained via molecular beam studies. This disagreement suggests that the spin-rotation mechanism for symmetric tops be reassessed, and two directions are immediately apparent. First, spin symmetry should be included and second, the correlation times should be studied. In particular, several different correlation times arise in the theoretical treatment of the spin-rotation mechanism for symmetric top molecules. These are usually approximated as being equal. Thus one effective correlation time is obtained from the T_1 minimum. Before, however, treating the collisional aspects and discussing the validity of this one correlation time approximation, the role of spin symmetry must be assessed. It is the purpose of this paper to discuss the nuclear magnetic relaxation of symmetric top molecules due to the spin-rotation mechanism with the inclusion of the spin symmetry of the

three off-axis spins. It is found that the expressions which include spin symmetry are the same as those obtained by BBH if the gas can be considered as an equilibrium mixture of the symmetry species and if the "zero" frequency term $K = -1$ to $+1$ is neglected. However, it is shown that neglecting the $K = -1$ to $+1$ term is not justified and leads to different effective spin-rotation coupling constants for the different species. As far as the spectral density terms are concerned, those which arise in the usual treatment (e.g., BBH) are not changed by additional weightings for different spin symmetries, and there are only small differences between the spectral density terms of BBH and the theory presented here due to different averages over rotational states. That spin symmetry plays a minor role for these terms is not obvious since, for example, the ortho and para species (of diatomic molecules relax, in general, at different rates (Sanctuary 1973). For symmetric tops with the X spins having a spin of $1/2$, the total off-axis spin of $I = 3/2$ and $1/2$ belong to different symmetry species and thus might have been expected to have different relaxation rates.

2. Symmetry Considerations

It is assumed that inversion of the symmetric top molecules is unimportant and classification

under the point group C_3 is sufficient. Moreover, only the X , off-axis, spins are treated since the Y spin is not affected by the C_3 symmetry. Consequently, the spins of atoms Y and Z are taken as arbitrary, or the Y atom may be considered as absent. Such molecules exist as three species, namely A , E_1 , and E_2 . For example, assuming

the X atoms to have spin $1/2$, the total spin of the X atoms is $3/2$ for A symmetry and $1/2$ for each of E_1 and E_2 symmetries. There is thus a relaxation tensor $(1/T)_i$, where $i = A, E_1, \text{ or } E_2$, for each species. Each relaxation tensor has C_{3v} symmetry, the group of the magnetic field, so that it can be written

$$[1] \quad \left(\frac{1}{T}\right)_i = \left(\frac{1}{T_1}\right)_i e^{i(1)0} e^{i(1)0} - \left(\left(\frac{1}{T_2}\right)_i + i\gamma_i H \sigma_i \right) e^{i(1)1} e^{i(1)-1} - \left(\left(\frac{1}{T_2}\right)_i - i\gamma_i H \sigma_i \right) e^{i(1)-1} e^{i(1)1}$$

$$= \bar{z} \bar{z} \left(\frac{1}{T_1}\right)_i + (\hat{x}\hat{x} + \hat{y}\hat{y}) \left(\frac{1}{T_2}\right)_i + (\hat{x}\hat{y} - \hat{y}\hat{x}) \gamma_i H \sigma_i$$

with respect to either a Cartesian or a spherical basis:

$$[2] \quad e^{i(1)0} = \bar{z}; \quad e^{i(1)\pm 1} = \mp(1/\sqrt{2})(\hat{x} \pm i\hat{y})$$

The scalars $(T_1^{-1})_i$, $(T_2^{-1})_i$, and σ_i (Chen and Snider 1967) have their usual meanings.

The existence of three species may be detectable as a nonexponential relaxation, e.g.

$$[3] \quad \langle I_z \rangle(t) - \langle I_z \rangle_{\text{eq}} = e^{-i(\omega_2)t} (\langle I_z \rangle_A(0) - \langle I_z \rangle_{\text{eq},A}) + e^{-i(\omega_1)t} (\langle I_z \rangle_{E_1}(0) - \langle I_z \rangle_{\text{eq},E_1})$$

$$+ e^{-i(\omega_2)t} (\langle I_z \rangle_{E_2}(0) - \langle I_z \rangle_{\text{eq},E_2})$$

the notation being obvious. This assumes that the conversion rate between the species is slow with respect to the relaxation rates. Furthermore it is well known that for A symmetry, the K values of $3n$ only exist (for integral n), while E_1 and E_2 symmetries have respectively values of $3n-1$ and $3n-1$. Here K is the projection of the rotational angular momentum J on the symmetry axis of the molecule. Consequently the total spin of the X atoms and the K rotational quantum number are symmetry related.

It is possible to symmetry adapt the spin and rotational functions to take advantages of the C_3 symmetry (see, e.g., Townes and Schawlow 1955). The group C_3 has three one-dimensional irreducible representations. In spin space these can be labelled by s so that for a symmetry adapted spin function Ψ_s

$$[4] \quad P_{123} \Psi_s = \epsilon^s \Psi_s$$

where P_{123} is the cyclic permutation of spins (right hand rule about the symmetry axis assigns a definite direction to the symmetry axis) while $\epsilon = \exp(2\pi i/3)$. The value $s = 0$ designates A symmetry, $s = +1$ is E_1 , while $s = -1$ is E_2 . The projection P_s onto spin symmetry species s is then given by

$$[5] \quad P_s = \frac{1}{3}(1 + \epsilon^{-s} P_{123} + \epsilon^s P_{321})$$

It is useful to express the projection operator P_s in terms of spin operators. For spin $1/2$ nuclei (Sanctuary 1971) this becomes

$$[6] \quad P_s = \frac{1}{3}[1 + \cos(2\pi s/3)(I(I+1) - \frac{3}{2}) + 4 \sin(2\pi s/3)I_1 \times I_2 \cdot I_3]$$

where $I = I_1 + I_2 + I_3$.

Projection operators onto the symmetric top rotational energy levels are given by

$$[7] \quad P_{JK} = \sum_M |JKM\rangle \langle JKM|$$

where $|JKM\rangle$ denotes the symmetric top wave function. Since the X atoms are either bosons or fermions, a cyclic permutation of the atoms must leave the total wave function invariant. This leads

to the condition

$$K - s = 3n$$

[8] where n is an integer.

For the spin-rotation mechanism, the Hamiltonian for the X spins can be written

$$[9] \quad \mathcal{H}_{SR} = -2\pi\hbar \sum_{i=1}^3 I_i \cdot C_i \cdot J = -6\pi\hbar \sum_{s''=-1}^{+1} (I)^{s''} \cdot (C)^{-s''} \cdot J$$

where I_i is the i th nuclear spin operator and C_i is the spin-rotation coupling tensor for the i th nucleus. The symmetrized quantities

$$[10] \quad (C)^s = \frac{1}{3}(C_1 + \varepsilon^s C_2 + \varepsilon^{-s} C_3)$$

and

$$[11] \quad (I)^s = \frac{1}{3}(I_1 + \varepsilon^s I_2 + \varepsilon^{-s} I_3)$$

are defined in a manner similar to [5]. This Hamiltonian is now written in a spherical basis. Starting with the Cartesian expression for C_1 of Dong and Bloom (1970)

$$[12] \quad C_1 = \hat{x}\hat{x}C_{xx} + \hat{y}\hat{y}C_{yy} + \hat{z}\hat{z}C_{zz} + (\hat{x}\hat{z} + \hat{z}\hat{x})C_{xz}$$

where \hat{x} , \hat{y} , and \hat{z} denote the molecule fixed axes, C_2 and C_3 can be obtained by rotation about the symmetry axis by respectively $2\pi/3$ and $4\pi/3$. After some rearrangement, and after transforming to the laboratory frame by means of the rotation matrices \mathcal{D}_{MK}^J (Edmonds 1960), the Hamiltonian is found to be

$$[13] \quad \mathcal{H}_{SR} = -6\pi\hbar \sum_{s''=-1}^{+1} \left[C_s \sum_q (I)^{-s''+q} J^{-q} (-1)^q \delta_{s'',0} \right. \\ \left. - \sqrt{5} \sum_{q_1, q_2} (-1)^q \begin{pmatrix} 2 & 1 & 1 \\ -q & q_1 & q_2 \end{pmatrix} (C)^{s'',-q} J^{q_1} (I)^{-s''+q_1} \right]$$

The orientation of the molecule appears implicitly in

$$[14] \quad (C)^{s,q} \equiv \sum_l C_l \mathcal{D}_{-ql}^{-2} (\delta_{l,s} + \delta_{l,-2s})$$

through the rotation matrices, while

$$[15] \quad C_s = \frac{1}{3}(C_{xx} + C_{yy} + C_{zz})$$

The C_l coefficients are defined as

$$[16] \quad C_0 = (1/\sqrt{6})[\frac{1}{2}(C_{xx} + C_{yy}) - C_{zz}] \equiv (1/\sqrt{6})C_d$$

$$[17] \quad C_{\pm 1} = \pm C_{xz}$$

and

$$[18] \quad C_{\pm 2} = -\frac{1}{2}(C_{xx} - C_{yy}) \equiv -C_A$$

In [13] the superscripts q refer to the spherical components in the laboratory frame:

$$[19] \quad J^0 = J_z; \quad J^{\pm 1} = \mp(1/\sqrt{2})(J_x \pm iJ_y)$$

$$[20] \quad I^0 = I_z; \quad I^{\pm 1} = \mp(1/\sqrt{2})(I_x \pm iI_y)$$

and

$$[21] \quad (I)^{s,q} = \frac{1}{3}(I_1^q + \varepsilon^s I_2^q + \varepsilon^{-s} I_3^q)$$

3. Relaxation Expressions

The derivation of the relaxation tensor is now discussed and since it follows closely that recently presented for ortho-para diatomics (Sanctuary 1973), the details are omitted. The point at which spin symmetry arises is in the traces over the spin and rotational states. Since the K quantum number and the nuclear spin states are related, it is not possible to separate the two. To see explicitly where this occurs, the treatment of BBH is recalled. Three different correlation functions arise, one of which is (see BBH, [B12])

$$[22] \quad \langle \mathcal{D}_{-q, l}^{-2}(0) J^{q, l}(0) J^{q, l}(\tau) \mathcal{D}_{-q, l}^{-2}(\tau) \rangle = [\langle \mathcal{D}_{-q, l}^{-2}(0) J^{q, l}(0) J^{q, l}(\tau) \mathcal{D}_{-q, l}^{-2}(\tau) \rangle]_{\text{rot}, \mathcal{R}_{23}(\tau)}$$

which has been written in terms of the free correlation function and the reduced correlation function $\mathcal{R}_{23}(\tau)$. By including spin symmetry, the expression [22] is changed to

$$[23] \quad \langle (I)^{-s', s''} \mathcal{D}_{-q, l}^{-2}(0) J^{q, l}(0) J^{q, l}(\tau) \mathcal{D}_{-q, l}^{-2}(\tau) (I)^{-s, s'} \rangle \\ \times \sum_{J, K, K'} \mathcal{F}(s, s', s'') [\langle P_{JK} \mathcal{D}_{-q, l}^{-2}(0) J^{q, l}(0) J^{q, l}(\tau) \mathcal{D}_{-q, l}^{-2}(\tau) P_{JK} \rangle] \delta_{K, 3s+1} \delta_{K', 3s'+1} \mathcal{R}_{23}(\tau)$$

where the spin trace is

$$[24] \quad \mathcal{F}(s, s', s'') \equiv \text{tr}_{\text{spin}}(I)^{-s', s''} P_s(I)^{s', s} P_s(-1)^s \\ = \frac{2}{3} [1 + \frac{1}{2} \cos(2\pi s/3) (1 + 2 \cos(2\pi s''/3))] \delta_{s, s'+s''}$$

It has been assumed in [23] that collisions are ineffective in changing the spin states and all high frequency terms have been dropped ($\Delta J = \Delta K = 0$, except for $K = \pm 1$ with $\Delta K = \mp 2$). By use of the relation between K and s , [24] becomes

$$[25] \quad \mathcal{F}(s, s', s'') = \mathcal{F}(K, K', K'') = \frac{2}{3} [1 + \frac{1}{2} \cos(2\pi K/3) (1 + 2 \cos(2\pi K''/3))] \delta_{K, K'+K''}$$

Notice that when $s'' = 0$, no K transitions can occur. The second equality in [24] and [25] follows from the use of [6] and performing the spin trace (see Appendix). The rotational traces have been calculated by BBH and will not be reproduced here. The relaxation tensor is found to be, ignoring high frequency terms (i again refers to the A , E_1 , or E_2 species),

$$[26] \quad \left(\frac{1}{T} \right)_i = \frac{9 \cdot 6 \cdot 4 \pi^2 C_u^2}{H(J+1)(2J+1)} \sum_{\mu, \nu, s'} \begin{pmatrix} 1 & 1 & 1 \\ \mu & -\nu & \mu & \nu \end{pmatrix} \sum_{J, K, K'} p_{JK} J(J+1) \\ \times \mathcal{F}(K, K', K'') \mathcal{F}_{J, J, K', s'} \omega^{\mu+\nu} [(\mu+\nu)\omega]$$

where $\omega = \omega_j - \omega_{j'}$ and

$$[27] \quad \mathcal{F}_{J, K, K', s'} \omega^{\mu+\nu} \equiv \left\{ \frac{\tau_{11}}{1 + i\sigma\omega\tau_{11}} - \frac{3}{2} \left(\frac{C_d}{C_u} \right) \left(\frac{3K^2 - J(J+1)}{J(J+1)} \right) \frac{\tau_{12}}{1 + i\sigma\omega\tau_{12}} \right. \\ \left. + \frac{1}{6} \left(\frac{C_d}{C_u} \right)^2 \left(\frac{3K^2 - J(J+1)}{J(J+1)} \right)^2 \frac{\tau_{22}}{1 + i\sigma\omega\tau_{22}} \right\} \delta_{s', 0} \delta_{K, K'} \delta_{K, 3s+s'} \\ + \frac{1}{4} \frac{p_{JK}}{p_{JK}} |C_d|^2 (\delta_{K, 1} \delta_{K', 3s+1} \delta_{K, K'} + \delta_{K, -1} \delta_{K', 3s+1} \delta_{K, K'}) \frac{\tau_{22}'}{1 + i\sigma\omega\tau_{22}'}$$

The first term is the usual contribution that arises when J and K transitions are ignored. The second term accounts for the $K = -1$ to $+1$ and $K = +1$ to -1 , zero frequency, contribution. In [26], A symmetry corresponds to $s = 0$, E_1 symmetry to $s = +1$, and E_2 symmetry to $s = -1$.

The quantities τ_{ij} may be interpreted in the same way as done by BBH¹. The expressions for $(1/T_1)_i$, $(1/T_2)_i$, and the intermolecular chemical shift σ_i , are found by taking μ appropriately. For

¹The notation is slightly different from that used by BBH: $\tau_{11} = \tau_1$, $\tau_{12} = \tau_{12}$, $\tau_{22} = \tau_2$. The prime on the τ_{22}' in the last term of [27] indicates that the relaxation time for $K = -1$ to $+1$ differs from τ_{22} .

$1/T_1, \mu = 0$ (see [1]) and with $I = 3/2$ and $s = 0$, the relaxation time for A symmetry is

$$[28] \quad \left(\frac{1}{T_1}\right)_A = \frac{8\pi^2}{3} C_a^2 \sum_{J=0}^{\infty} \sum_{K=-J}^J p_{JK}^A \delta_{K,3n} J(J+1) \left\{ \frac{\tau_{11}}{1 + \omega^2 \tau_{11}^2} - \frac{1}{2} \left(\frac{C_d}{C_a}\right) \left(\frac{3K^2 - J(J+1)}{J(J+1)}\right) \frac{\tau_{12}}{1 + \omega^2 \tau_{12}^2} + \frac{1}{6} \left(\frac{C_d}{C_a}\right)^2 \left(\frac{3K^2 - J(J+1)}{J(J+1)}\right)^2 \frac{\tau_{22}}{1 + \omega^2 \tau_{22}^2} \right\}$$

The E_1 and E_2 rates are found by setting $I = 1/2$ and s to respectively -1 and $+1$. The result is

$$[29] \quad \left(\frac{1}{T_1}\right)_{E_{1,2}} = \frac{8\pi^2}{3} C_a^2 \sum_{J=0}^{\infty} \sum_{K=-J}^J p_{JK}^{E_{1,2}} \delta_{K,3n-1} J(J+1) \{ \dots \} + \frac{8\pi^2}{3} |C_d|^2 \sum_{J=0}^{\infty} p_{J1}^{E_{1,2}} J(J+1) \frac{\tau_{22}}{1 + \omega^2 \tau_{22}^2}$$

The quantities in the curly brackets in [28] and [29] are the same, and the only difference in the two equations is the restrictions on the K sums and the presence in the latter expression of the $K = -1$ to $+1$ term. It should be pointed out that the partition functions also have the K averages restricted by symmetry, so that the Boltzmann weights are

$$[30] \quad p_{JK}^i = (2J+1) e^{-\epsilon_{JK}} / \sum_{J=0}^{\infty} \sum_{K=-J}^J (2J+1) \delta_{K,3n+s} e^{-\epsilon_{JK}} \equiv (2J+1) e^{-\epsilon_{JK}} / Q^i$$

where

$$[31] \quad \epsilon_{JK} = \alpha J(J+1) + \beta K^2$$

and

$$[32] \quad \alpha = B/kT; \quad \beta = (A - B)/kT$$

are the rotation constants.

Since negative and positive values of K are allowed, the restricted K averages for E_1 and E_2 run over exactly the same values. Hence it follows that

$$[33] \quad (1/T_1)_{E_1} = (1/T_1)_{E_2}$$

Finally the expressions for $(1/T_2)_i$ are found by replacing the Lorentzians in [28] and [29] by

$$[34] \quad \frac{1}{2} [\tau_{ij} + \tau_{ij}/(1 + \omega^2 \tau_{ij}^2)]$$

4. Discussion

The expression obtained by BBH for $1/T_1$ due to the spin-rotation mechanism is

$$[35] \quad \frac{1}{T_1} = \frac{8\pi^2}{3} C_a^2 \sum_{J=0}^{\infty} \sum_{K=-J}^J \frac{J(J+1)(2J+1) e^{-\epsilon_{JK}}}{Q_r} \left\{ \frac{\tau_{11}}{1 + \omega^2 \tau_{11}^2} - \frac{1}{2} \left(\frac{C_d}{C_a}\right) \left(\frac{3K^2 - J(J+1)}{J(J+1)}\right) \frac{\tau_{12}}{1 + \omega^2 \tau_{12}^2} + \frac{1}{6} \left(\frac{C_d}{C_a}\right)^2 \left(\frac{3K^2 - J(J+1)}{J(J+1)}\right)^2 \frac{\tau_{22}}{1 + \omega^2 \tau_{22}^2} \right\}$$

where there are no K restrictions and Q_r is

$$[36] \quad Q_r = \sum_{J=0}^{\infty} \sum_{K=-J}^J (2J+1) e^{-\epsilon_{JK}}$$

This result can be obtained if the $K = -1$ to $+1$ term is neglected, and one third of the K levels are assumed to be associated with $I = 3/2$ and the other two thirds of the K levels with $I = 1/2$. With these approximations and with the relation

[37]

$$Q^2 \cong \frac{1}{3} Q,$$

it follows that

[38]

$$(1/T_1) \cong (1/T_1)_A \cong (1/T_1)_{E_1} = (1/T_1)_{E_2}$$

The validity of [38] is now discussed with respect to the assumption of (1) equal partitioning of the K levels per nuclear spin state and (2) neglecting the $K = -1$ to $+1$ term. The relaxation rates are written as

[39]

$$(1/T_1)_i = (4\pi^2/\alpha)(C_{\text{eff}}^2)_i \tau / (1 + \omega^2 \tau^2)$$

with the assumption that $\tau = \tau_{11} = \tau_{12} = \tau_{22} = \tau_{23}$. The effective coupling constant is

[40]

$$(C_{\text{eff}}^2)_i = k_1^2 C_a^2 + k_2^2 C_b C_c + k_3^2 C_d^2 + k_4^2 C_d^2$$

where

[41]

$$k_1^4 = \frac{2\alpha}{3} \sum_{J=0}^{\infty} \sum_{K=-J}^J \frac{(2J+1) \exp[-\epsilon_{JK}]}{Q^4} J(J+1) \delta_{K,3n}$$

[42]

$$k_2^4 = \frac{-4\alpha}{9} \sum_{J=0}^{\infty} \sum_{K=-J}^J \frac{(2J+1) \exp[-\epsilon_{JK}]}{Q^4} (3K^2 - J(J+1)) \delta_{K,3n}$$

[43]

$$k_3^4 = \frac{2\alpha}{27} \sum_{J=0}^{\infty} \sum_{K=-J}^J \frac{(2J+1) \exp[-\epsilon_{JK}]}{Q^4} \frac{(3K^2 - J(J+1))^2}{J(J+1)} \delta_{K,3n}$$

The expressions for $k_i^{E_1} = k_i^{E_2}$ are obtained from above by replacing Q^4 by Q^{E_1} and $\delta_{K,3n}$ by $\delta_{K,3n+1}$. The $K = -1$ to $+1$ term is given by

[44]

$$k_4^{E_1} = k_4^{E_2} = \frac{2}{3} \alpha \sum_{J=0}^{\infty} \frac{(2J+1) \exp[-\alpha J(J+1)]}{Q^{E_1}} J(J+1)$$

Finally the expressions for k_i ($i = 1, 3$) from the BBH expression in [35] can be obtained from [41]–[43] by dropping the $\delta_{K,3n}$ and replacing Q^4 by Q_c .

For many symmetric top molecules the J, K level spacings are small enough so that $\alpha, \beta \ll 1$ at usual temperatures. Hence it is possible to replace the averages over J and K by integrations. Hence the k_i 's in the BBH expression (no K restrictions) can be approximated by (Armstrong and Courtney 1972; Dong and Bloom 1970; Dong 1968)

[45]

$$k_1 \cong 1 - y^2/3$$

[46]

$$k_2 \cong -(4/9)y^2$$

[47]

$$k_3 \cong [(1 - y^2)/y^2](s - 1 - y^2/3) - 1/9 + (5/27)y^2$$

where

[48]

$$s = (1/2y) \ln [(1+y)/(1-y)], \quad \beta > 0$$

$$= (1/|y|) \tan^{-1} |y|, \quad \beta < 0$$

and

[49]

$$y = [\beta/(\alpha + \beta)]^{1/2}$$

The coefficient $k_4^{E_1}$ is also approximated in this way by

[50]

$$k_4^{E_1} \cong 2 e^{-\beta/\alpha} [(\alpha + \beta)/\pi]^{1/2}$$

These different k_i 's are given in Table 1 for several different symmetric tops treated by Armstrong and Courtney (1972). Table 2 lists the rotational constants for these molecules. In Table 1 for each molecule the first line gives the integrated values obtained from [45]–[47]. The second line gives the

TABLE 1. Coefficients in the equation for C_{rot}^2 calculated at 293 K. \int —integrated over all J and K (cf. Armstrong and Courtney 1972); Σ —exact sum over all J and K to $J = 100$; A —exact sum over all J and $K = 3n$ to $J = 100$; E_i —exact sum over all J and $K = 3n + 1$ to $J = 100$

	k_1	k_2	k_3	k_4	C_{rot}^2 (kHz) ²
BF₃					
\int	1.331	-0.442	0.177	—	32.0
Σ	1.329	-0.441	0.177	—	32.0
A	1.330	-0.441	0.178	—	32.1
E_1	1.330	-0.441	0.178	0.0333 (0.0331)	—
CHF₃					
\int	1.282	-0.376	0.161	—	63.7
Σ	1.280	-0.376	0.163	—	63.4
A	1.282	-0.376	0.163	—	63.4
E_1	1.282	-0.376	0.163	0.0342 (0.0342)	—
CH₃F					
\int	0.724	0.365	0.060	—	4.81
Σ	0.721	0.370	0.060	—	4.34
A	0.721	0.370	0.060	—	4.34
E_1	0.721	0.370	0.060	0.174 (0.175)	—
PH₃					
\int	1.046	-0.061	0.104	—	65.1
Σ	1.040	-0.058	0.097	—	64.7
A	1.040	-0.058	0.097	—	64.7
E_1	1.040	-0.058	0.097	0.156 (0.157)	—
NH₃					
\int	1.192	-0.262	0.142	—	237.2
Σ	1.182	-0.250	0.132	—	233.2
A	1.183	-0.250	0.131	—	233.2
E_1	1.183	-0.250	0.133	0.200 (0.205)	243.1

TABLE 2. Rotational constants for several symmetric top molecules and the values of α and β at 293 K (Townes and Schawlow 1955)

	B(MHz)	A(MHz)	$\alpha \times 10^3$	$\beta \times 10^3$
BF ₃	10 640	5 335	1.743	-0.884
CHF ₃	10 348	5 600	1.695	-0.777
CH ₃ F	25 469	152 650	4.172	20.872
PH ₃	133 478	118 000	21.864	-2.530
NH ₃	298 043	183 178	48.820	-17.883

exactly summed value up to $J = 100$. The third and fourth lines give k_i^A and $k_i^{E_1}$ again summed up to $J = 100$, while the value in brackets for $k_4^{E_1}$ gives the integrated value [50]. The close agreement between the values confirms the validity of integrating over J and K when $\alpha, \beta \ll 1$ and show that there is very little difference between k_i^A and $k_i^{E_1}$. In fact, for these molecules the coefficients have been calculated down to their boiling points at 1 atm and only negligible differences occur between k_i^A and $k_i^{E_1}$ ($i = 1, 3$). It can be concluded that both integration and the assumption of equipartitioning of the K states per spin state are excellent approximations.

Turning now to an assessment of the approximation of neglecting the $K = -1$ to $+1$ terms, it is seen from Table 1 that $k_4^{E_1}$ is not small, and that to a good approximation it can be approximated by integrations. Moreover, $k_4^{E_1}$ is temperature dependent in contrast to the other k_i 's and it reaches a maximum at

[51]

$$T_{max} = 2A/k.$$

TABLE 3. Spin rotation constants in kHz for several symmetric tops from molecular beam data*

	Nucleus	C_A	C_B	C_C
BF_3^a	F	5.5	6.0	—
CHF_3^a	F	7.5	4.0	—
CH_3F^b	H	5.4	-13.9	—
PH_3^c	H	7.9	0.34	—
NH_3^c	H	-12.5	10.65	7.05

* Given by Foltz (1970)^a, Wolley *et al.* (1971)^b, Davis *et al.* (1971)^c, and Gordon (1955)^d.

Since, for the symmetric tops in Table 2 T_{rot} falls in the liquid or solid regime, it can be safely stated that for gases this term increases with decreasing temperatures. The total contribution from this term to relaxation depends on the relative values of C_A , C_B , and C_C . The values of C_A and C_B are known for the five symmetric top molecules treated here and are given in Table 3. The data for calculating C_C was only found for NH_3 (Gordon 1955) and is comparable in absolute value with $|C_B|$ and $|C_A|$. The effective coupling constant, C_{eff}^2 , has been calculated for NH_3 using these values of C_A , C_B , and C_C and is given in Table 1. Clearly a considerable difference occurs between the value for the A species and the $E_{1,2}$ species. Unfortunately, it was not possible to compare the effective coupling constants for the other molecules since C_C is not known. The value for C_{eff}^2 for the $E_{1,2}$ species is not given therefore for these molecules in Table 1. However, if NH_3 is representative, it may be surmised that the $K = -1$ to $+1$ term is important and should be measurable in these molecules. In fact, when α and $\beta \ll 1$, the difference between the relaxation of the A and $E_{1,2}$ species would make it possible to obtain the relative values for $|C_{\text{ax}}|$ and $|C_{\text{yz}}|$ directly from NMR measurements. Lower temperatures should enhance the effect.

The motivation behind this work was to attempt to rationalize the differences between the molecular beam and NMR values for C_{eff}^2 and hence the effective cross sections, σ_{eff} . Although the spin symmetry aspects discussed in this paper bring out interesting features, they cannot resolve this disagreement. In fact if the $k_4^{E_1}$ term is included, C_{eff}^2 becomes larger, whereas the NMR results indicate they should be smaller. Moreover if any other mechanism were important, it would have to dominate the spin-rotation mechanism, again requiring a larger coupling coefficient than is observed. Hence it can be surmised that the answer still lies in an error in the treatment of the spin-rotation mechanism. In particular the approximation of assuming a single $\tau = \tau_{1,1} = \tau_{1,2} = \tau_{2,2} = \tau_{2,1}$ requires a full assessment and such a program is presently underway.

Appendix

The spin trace

$$[\text{A1}] \quad \mathcal{J}(s, s', s'') = \text{tr}_{\text{spin}} (I)^{-s''} \cdot P_A(I)^{s''} P_B(I)^s$$

becomes

$$[\text{A2}] \quad \mathcal{J}(s, s', s'') = \frac{1}{8} \text{tr}_{\text{spin}} (I)^{-s''} \cdot (I)^{s''} P_C \delta_{s,s'+s''}$$

by using definitions [5] and [11]. For spin 1/2 nuclei, the contraction of the spin operators gives

$$[\text{A3}] \quad (I)^{-s''} \cdot (I)^{s''} = \frac{1}{3}(9/4 + \cos(2\pi s''/3)(I(I+1) - 9/4))$$

where I is the total nuclear spin of the three off-axis nuclei. Combining [A3] and [6] gives:

$$[\text{A4}] \quad \mathcal{J}(s, s', s'') = 1/81 \text{tr}_{\text{spin}} [(9/4 + \cos(2\pi s''/3)(I(I+1) - 9/4)) \times (1 + \cos(2\pi s'/3)(I(I+1) - 7/4)) \delta_{s,s'+s''}]$$

The last term in the projection operator in [6] is odd in I_z and traces to zero. The trace over the total nuclear spin with $I = 3/2$ and $1/2$ can now be performed to give:

$$[\text{A5}] \quad \mathcal{J}(s, s', s'') = \frac{1}{9} [1 + \frac{1}{2} \cos(2\pi s'/3)(1 + 2 \cos(2\pi s''/3))] \delta_{s,s'+s''}$$

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- ARMSTRONG, R. L. and COURNEY, J. A. 1972. *Can. J. Phys.* **50**, 1262.
- BLOOM, M., BRIDGES, F., and HARDY, W. N. 1967. *Can. J. Phys.* **45**, 3533.
- CHEN, F. M. and SNIDER, R. F. 1967. *J. Chem. Phys.* **46**, 3937.
- DAVIS, P. B., NEUMANN, R. M. N., WOPSY, S. C., and KLEMPERER, W. 1971. *J. Chem. Phys.* **55**, 3564.
- DONG, R. 1968. Ph.D. Thesis, University of British Columbia, Vancouver, British Columbia. Unpublished.
- DONG, R. and BLOOM, M. 1970. *Can. J. Phys.* **48**, 793.
- EDMONDS, A. E. 1960. *Angular momentum in quantum mechanics* (Princeton University Press, Princeton).
- FOLLETT, T. L. 1970. Ph.D. Thesis, Harvard University, Cambridge, Mass.
- GORDON, J. P. 1955. *Phys. Rev.* **99**, 1253.
- MCCOURT, F. R. and HESS, S. 1970. *Z. Naturforsch. a*, **25**, 1169.
- 1971. *Z. Naturforsch. a*, **26**, 1234.
- SANCTUARY, B. C. 1971. Ph.D. Thesis, University of British Columbia, Vancouver, British Columbia. Unpublished.
- 1973. *Can. J. Phys.* **51**, 2488.
- TOWNES, C. H. and SCHAWLOW, A. L. 1955. *Microwave spectroscopy* (McGraw-Hill Book Company, New York).
- WOPSY, S. C., MUENTER, J. S., and KLEMPERER, W. 1971. *J. Chem. Phys.* **55**, 2074.