

On the Intramolecular Quadrupole Mechanism of Nuclear Magnetic Relaxation in the Gas Phase

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By use of a nuclear quadrupole intramolecular mechanism, expressions are obtained for the relaxation rates for both ortho and para X_2 molecules which have nuclear spins $I_1 > 1/2$. It is found, except for $I_1 = 1$, that as a result of the nuclear spin weightings the two species relax with different rates, even at temperatures high enough so that the rotational averages are approximately equal.

Par l'utilisation d'un mécanisme nucléaire intra-moléculaire de quadrupole des expressions sont obtenues pour les taux de relaxation de chacune des molécules ortho et para X_2 ayant des spins nucléaires $I_1 > 1/2$. On trouve qu'à l'exception du cas $I_1 = 1$, les deux types de molécules possèdent des taux de relaxation différents, même à des températures suffisamment élevées pour que les moyennes rotationnelles soient approximativement égales. [Traduit par le journal]

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I. Introduction

Homonuclear diatomic molecules which possess nuclear spins exist as ortho and para species. Since conversion times between these two species in the gas phase can be very much longer than the time for a nuclear magnetic relaxation experiment, it is possible that a two-relaxation process might be observed. Assuming that the characteristic decay time of the rotational states is the same in both species, *i.e.* the correlation time for ortho and para is assumed equal, there are two possibilities in which a two-relaxation process can occur. Firstly, a difference can arise at temperatures where the averages over odd and even rotational states lead to different spectral density terms. Such a situation has been reported (Hardy 1964) for ortho-para- D_2 . Secondly, a phenomenological difference may occur as a result of different nuclear spin weightings for ortho and para X_2 molecules. One species will always have different total spin contributions, as well as different

transitions between the spin states, than the other species. It is this second point that is treated in this paper.

When the atoms have nuclear spins of $1/2$, only a one-relaxation process can arise. Hence nuclear spins greater than $1/2$ are treated. Moreover, since nuclear spin relaxation in gases of molecules with spins greater than $1/2$ is dominated by quadrupole intramolecular processes, only this mechanism is considered.

In Sect. II some phenomenological aspects are reviewed, while Sect. III forms the main body of the paper dealing with the derivation of the relaxation tensor in this case. A discussion concludes the formal structure of the paper.

II. Macroscopic Equations

It is assumed that the magnetization results only from the nuclear dipole moments and that higher order moments are negligible. Thus the relaxation is given by the Bloch equations:

$$[1] \quad \frac{\partial \langle I \rangle}{\partial t} + \gamma_I H \times \langle I \rangle = -\frac{1}{T} (\langle I \rangle - \langle I \rangle_{eq})$$

where H is the magnetic field, γ_I is the gyromagnetic ratio, and $\langle I \rangle$ and $\langle I \rangle_{eq}$ are respectively the nonequilibrium and equilibrium nuclear spin polarizations which result from the sum of the spins on the two nuclei, $I = I_1 + I_2$. The relaxation tensor is $1/T$ and depending on the component of the polarization, it gives the longitudinal, $1/T_1$, and transverse, $1/T_2$, relaxation rates and the intermolecular chemical shift σ (Chen and Snider 1967):

$$\begin{aligned}
 [2] \quad \frac{1}{T} &= e^{iI_1 0} e^{iI_2 0} \frac{1}{T_1} - \left(\frac{1}{T_2} + i\gamma_{I_1} H\sigma \right) e^{iI_1 1} e^{iI_2 -1} - \left(\frac{1}{T_2} - i\gamma_{I_1} H\sigma \right) e^{iI_1 -1} e^{iI_2 1} \\
 &= \frac{1}{T_1} + (\hat{x}\hat{x} + \hat{y}\hat{y}) \frac{1}{T_2} + (\hat{x}\hat{y} - \hat{y}\hat{x})\gamma_{I_1} H\sigma
 \end{aligned}$$

Both a Cartesian and spherical basis,

$$[3] \quad e^{iI_1 0} = 2 \quad \text{and} \quad e^{iI_1 -1} = \mp (1/\sqrt{2})(\hat{x} \pm i\hat{y})$$

are used in [2] with the field along the \hat{z} axis, $H = 2H_1$. For relaxation of X_2 molecules, the relaxation tensor can be separated into ortho (o) and para (p) terms. Since in general the rates are different, a two-relaxation process is possible, e.g.,

$$[4] \quad \langle I_z \rangle(t) - \langle I_z \rangle_{\text{eq}} = e^{-t/(T_1)^o} (\langle I_z \rangle_o(0) - \langle I_z \rangle_{\text{eq},o}) + e^{-t/(T_1)^p} (\langle I_z \rangle_p(0) - \langle I_z \rangle_{\text{eq},p})$$

The simplest examples, ortho- and para- D_2 , have total spins of $I = 1$ and 0 with corresponding J levels restricted to being odd and even respectively. Of course in this case $(1/T)_p$ vanishes. However, for para- D_2 (or N_2), $I = 1$ and for the ortho species, $I = 0$ and 2 with symmetry restrictions on associated J levels being odd and even. The possibility arises for $I = 0$ to 2 transitions. The contribution to the relaxation tensor can be generally written,

$$[5] \quad (1/T)_s = \sum_{I=0}^{2I_1} (1/T)_{II} + 2 \sum_{I>I'=0}^{2I_1} (1/T)_{II'}$$

where the s denotes the species, ortho or para, and the sums are over only those even or odd values of I and I' as required by symmetry (this is denoted by Σ'). The first term accounts for the contribution to relaxation due to a given I , while the second denotes the contribution which arises from transitions between different I levels. Hence the relaxation of one species can be thought of as a matrix in $I-I'$ index space, e.g., for ortho- D_2 this is:

$$[6] \quad (1/T)_{o-D_2} = \begin{pmatrix} 0 & (1/T)_{02} \\ (1/T)_{20} & (1/T)_{22} \end{pmatrix}$$

At this stage, the terms $(1/T)_{II'}$ have symbolic meanings only and the exact definitions are given in the following section.

III. Evaluation of the Relaxation Tensor

One starting point for the derivation of all nuclear spin relaxation phenomena in gases is

$$[7] \quad 1/T = \langle \hat{I} | \mathcal{L}_z (\mathcal{R} + i\mathcal{L}_{\text{eff}})^{-1} \mathcal{L}_z | \hat{I} \rangle; \langle \hat{I} | \hat{I} \rangle$$

This can be obtained from either a generalized master equation (correlation theory approach) or from a Boltzmann equation (kinetic theory approach), both being essentially equivalent (Sanctuary 1971; Sanctuary and Snider 1973). The meanings for the various terms follow:

(1) The inner product in [7] is defined by

$$[8] \quad \langle A | B \rangle = \text{tr} (A^\dagger \rho_0 B)$$

where ρ_0 is the equilibrium density operator,

$$[9] \quad \rho_0 = \exp(-\mathcal{H}_{\text{int}}/kT) / \text{tr} \exp(-\mathcal{H}_{\text{int}}/kT)$$

and \mathcal{H}_{int} is the internal Hamiltonian given by

$$[10] \quad \mathcal{H}_{\text{int}} = BJ^2 + \omega_I I_z + \omega_J J_z + \mathcal{H}_Q$$

B is the rotational constant and at temperatures of usual experimental interest the last three terms can be dropped when used in [9]. The superscripts \dagger and \ddagger denote the tensor transpose and the

ordinary operator adjoint respectively; the tilde is the Kubo transform and the trace is to be taken over the spin, rotational, and translational states.

(2) The coupling Hamiltonian is in this case due to quadrupole interaction and for two identical nuclei is given by (Ramsey 1956, p. 421-422)

$$[11] \quad \mathcal{H}_c = -\frac{3}{2} \left(\frac{eqQ}{\hbar} \right) \left(\frac{1}{(2J+3)(2J-1)I_1(2I_1-1)} \right) \sum_q (-1)^q ([I_1]^{(2)q} + [I_2]^{(2)q}) [J]^{(2)-q}$$

where $[I_i]^{(2)q}$ and $[J]^{(2)q}$ are the spherical components of second-rank symmetric traceless tensors constructed from I_i ($i=1, 2$), namely $[I_i]^{(2)}$, and from the rotational operator J , namely $[J]^{(2)}$, respectively. Operating on an operator A , \mathcal{L}_c is defined as

$$[12] \quad \mathcal{L}_c A \equiv [\mathcal{H}_c, A]$$

for nuclear quadrupole coupling.

(3) The collision (super-) operator \mathcal{R} accounts for the effects of collisions on the rotational states. It is assumed that for both species only one equal relaxation time (or correlation time) arises. Thus \mathcal{R} can be replaced by $1/\tau$, which is equivalent to an exponential decay of the rotational state.

(4) The effective Liouville operator on an operator A is

$$[13] \quad \mathcal{L}_{eff} A = [(\omega_I - \omega_J) J_z, A]$$

where ω_I is the rotational Larmor frequency, $\omega_J = -\gamma_J \hbar H$, and ω_{I_1} is the nuclear Larmor frequency, $\omega_{I_1} = -\gamma_{I_1} \hbar H$. This term is discussed elsewhere (Sanctuary and Snider 1973) and accounts for transforming to the rotating frame of the molecule. The higher rotational frequency terms are ignored.

The situations where only one total nuclear spin, I , exists (I is a good quantum number) and the case where several I 's are present (I is not a good quantum number) are now discussed. In the former case, when only one nuclear spin exists, the total spin operator I appears in [7] as a normalized operator with respect to the inner product [8], *i.e.*

$$[14] \quad \langle \mathcal{P}_I I \cdot | \mathcal{P}_I I \rangle = 1$$

For this case, the normalized spin operator is

$$[15] \quad \hat{I} = \sqrt{3/I(I+1)} I$$

when the projection operator is defined by

$$[16] \quad \mathcal{P}_I \equiv \sum_{M_I} |IM_I\rangle \langle IM_I|$$

The quantity $|IM_I\rangle$ denotes a normalized nuclear spin state for the molecule. Note that the particular M_I level is not distinguished by this projection operator. It is not necessary to do so as a consequence of both the assumed linear Zeeman splitting and the Wigner-Eckart theorem. For example, if the coupling Hamiltonian is treated generally and written in terms of lattice, F^{Iq} , and spin, T^{Iq} , operators of tensor rank I and component q ,

$$[17] \quad \mathcal{H}_c = \sum_q F^{Iq} T^{Iq} (-1)^q$$

and I is written in a spherical basis as I^0 , namely $I^0 = I_z$ and $I^{\pm 1} = \mp I/\sqrt{2} (I_x \pm iI_y)$, then it is a simple matter to obtain from [7] the appropriate expression for $1/T_1$:

$$[18] \quad \frac{1}{T_1} = \frac{3}{I(I+1)} \langle \mathcal{H}_c^2 \rangle \sum_{q=-I}^I \frac{q^2 \tau}{1 + iq(\omega_I - \omega_J) \tau}$$

The commutation relation, $[T^{Iq}, I^0] = q T^{Iq}$ has been used and $\langle \mathcal{H}_c^2 \rangle$ is just the average over spin and lattice states of the coupling Hamiltonian. In fact, q is the difference between M_I levels,

but because linear Zeeman splitting has been assumed and because $\langle \mathcal{H}_c^2 \rangle$ is evaluated independent of the choice of basis, the total expression [18] is independent of M_I . The familiar form of [18] gives some insight to the more general form of [7].

The situation in which I is not a good quantum number is now discussed. In this case, it is necessary to project onto the ortho or para species rather than projecting onto states with fixed I . Denoting this projection operator by \mathcal{P}_s , [7] becomes

$$[19] \quad (1/T)_s = \langle \langle \mathcal{P}_s \hat{J} | \mathcal{L}_c (1/\tau + i\mathcal{L}_{eff})^{-1} \mathcal{L}_c | \mathcal{P}_s \hat{J} \rangle \rangle / \langle \langle \mathcal{P}_s \hat{1} | \mathcal{P}_s \hat{1} \rangle \rangle$$

for a particular species. Explicitly the projection operator is

$$[20] \quad \mathcal{P}_s = \sum'_{IM_I} |IM_I\rangle \langle IM_I| = \sum'_I \mathcal{P}_I$$

where the prime denotes the appropriate restriction on I as required for ortho or para species. Again it is not necessary to distinguish individual M_I levels for the same reasons as described above, but it is important to distinguish the total nuclear spin states which occur for the two species: Furthermore, when I is even, the state for which $I = 0$ does not exist. This requires a change in normalization of \hat{I} from that given in [15], namely¹

$$[21] \quad \hat{I} = \sqrt{3}I(I+1)\hat{I} \text{ for } I > 0, \text{ and } \hat{I} = 0 \text{ for } I = 0$$

The denominator of [19] is thus found to be

$$[22] \quad \langle \langle \mathcal{P}_s \hat{J} | \mathcal{P}_s \hat{J} \rangle \rangle = \sum'_{I \neq 0}^{2I+1} (2I+1) / \sum'_I (2I+1)$$

in the high temperature approximation and use of [8] and [9]. Since this factor always occurs in the denominator, it can be taken into account by simply disregarding $I = 0$ in the partition function.

By standard commutator relations,

$$[23] \quad \mathcal{L}_c \hat{I}^\mu = [\mathcal{H}_Q, \hat{I}^\mu]_- \\ = \frac{i}{20} \left(\frac{eqQ}{\hbar} \right) \left(\frac{3}{I(I+1)} \right)^{1/2} \left(\frac{6}{I_1(2I_1-1)(2J-1)(2J+3)} \right) \\ \times \sum'_\nu (-1)^\nu \sqrt{30} \begin{pmatrix} 2 & 1 & 2 \\ -\mu & -\nu & \mu & \nu \end{pmatrix} ([I_1]^{(2)\nu} + [I_2]^{(2)\nu}) [J]^{(2)\mu+1\nu}$$

is obtained. Upon operating on $\mathcal{L}_c \hat{I}^\mu$ with $(1/\tau + i\mathcal{L}_{eff})^{-1}$ and taking the inner product [8] with $\mathcal{L}_c \hat{I}^\nu$, the $\mu\nu$ th spherical component of the relaxation tensor is

$$[24] \quad \left(\frac{1}{T} \right)_{s\mu\nu} = \frac{9}{100} \left(\frac{eqQ}{\hbar} \right)^2 \sum'_{I \neq 0} \left(\frac{\bar{p}_I}{(2J+1)} \right) \left(\frac{3}{I(I+1)} \right) \left(\frac{1}{I_1(2I_1-1)(2J-1)(2J+3)} \right)^2 \\ \times \text{tr} \{ \mathcal{P}_s \mathcal{P}_s [J]^{(2)} [I_1]^{(2)} + [I_2]^{(2)} \odot^4 \mathcal{P}_s \mathcal{P}_s ([I_1]^{(2)} + [I_2]^{(2)}) [J]^{(2)} \} \\ \times (1 + \delta_{I',0}) \sum'_\nu 30 \begin{pmatrix} 2 & 1 & 2 \\ -\mu & -\nu & \mu & \nu \end{pmatrix}^2 \frac{\tau}{1 + i(\mu+\nu)(\omega_{I_1} - \omega_J)\tau}$$

The Kronecker delta arises because elimination of $I = 0$ ignores one of the $I = 0 \rightarrow 2$ contributions. This can be seen, for example, from [5]. The $(1 + \delta_{I',0})$ simply doubles the contribution from $I' = 0 \rightarrow 2$. The Boltzmann weight is given by

$$[25] \quad \bar{p}_I = (2J+1) \exp(-J(J+1)B/kT) / \bar{Q}$$

¹The author is indebted to Professor R. T. Snider for pointing out that the normalization of the ortho state cannot be accomplished with [15] alone, and use of [19] and the definition in [21] do in fact lead to correctly normalized ortho and para states.

where the partition function, \bar{Q} , follows from [9] and is

$$[26] \quad \bar{Q} = \sum_{J, J'=0}^{\infty} (2J+1)(2J'+1) \exp(-J(J+1)B/kT)$$

Note that the spin degeneracy is retained in \bar{Q} as discussed above. The projection operator onto J states is given by

$$[27] \quad \mathcal{P}_J = \sum_{M_J} |JM_J\rangle \langle JM_J|$$

where the rotational states are denoted by $|JM_J\rangle$. It is not possible to separate the trace over the rotational states from that over spin states since even though they commute, they are symmetry restricted. In the simple case here of ortho- and para- X_2 molecules, this is easily accounted for by assigning the appropriate J sum (even or odd) with the appropriate I and I' sums (even or odd). Obviously the I and I' sums are both either even or odd for a given J sum. These restrictions are denoted again by a prime on the summation.

For $\mu = 0$ the longitudinal relaxation time is obtained, while $\mu = \pm 1$ gives $1/T_2$ and σ as the real and imaginary parts of $(1/T)^{1/2}$. From here on only $1/T_1$ is given explicitly with $1/T_2$ and σ easily obtainable from [24] and the following evaluation of the traces. By use of

$$[28] \quad \text{tr } \mathcal{P}_J [J]^{(2)} \mathcal{P}_J [J]^{(2)} = (1/6)J(J+1)(2J+1)(2J+3)(2J-1)$$

[24] becomes for a particular species,

$$[29] \quad \left(\frac{1}{T_1}\right)_s = \frac{9}{200} \left(\frac{eqQ}{\hbar}\right)^2 \sum_{\substack{J, J', I, I' \\ J \neq 0}} \bar{P}_J \left(\frac{J(J+1)}{(2J-1)(2J+3)}\right) \left(I_1(2I_1-1)\right) \\ \times \frac{(1+\delta_{I,0})}{I(I+1)(2I+1)} T(I, I', I_1) \left[\frac{\tau}{1+(\omega_{I_1}-\omega_J)^2\tau^2} + \frac{4\tau}{1+4(\omega_{I_1}-\omega_J)^2\tau^2} \right]$$

The spin trace $T(I, I', I_1)$ is now evaluated. It is given by

$$[30] \quad T(I, I', I_1) = (1/5) \text{tr } \mathcal{P}_I ([I_1]^{(2)} + [I_2]^{(2)}) : \mathcal{P}_{I'} ([I_1]^{(2)} + [I_2]^{(2)}) \\ = \sum_{M_I M_{I'}} |\langle IM_I | [I_1]^{(2)M_I - M_{I'}} + [I_2]^{(2)M_I - M_{I'}} | I M_{I'} \rangle|^2$$

There are several ways to proceed. By noting in [29] that I' occurs (except for $\delta_{I,0}$) only in the projection operator, the sum over I' can be performed to give

$$[31] \quad \sum_{I'} T(I, I', I_1) = (1/3)I_1(2I_1-1)(2I_1+3)(I_1+1)(2I_1+1) \\ \times \left[1 + 2 \left(\frac{3/4 C_I(C_I+1) - I_1^2(I_1+1)^2}{I_1(I_1+1)(2I_1-1)(2I_1+3)} \right) \right]$$

where $C_I = I(I+1) - 2I_1(I_1+1)$ (see, e.g., Ramsey 1956, p. 423). The unsummed $T(I, I', I_1)$ can also be found by standard methods (see, e.g., Edmonds (1960, [7.1.7] and [7.1.8]) or Rose (1957, [6.25])). The result is

$$[32] \quad T(I, I', I_1) = 2(1 + (-1)^{I+I'}) (2I+1)(2I'+1) \begin{Bmatrix} I & 2 & I' \\ I_1 & I_1 & I_1 \end{Bmatrix}^2 (I_1 || [I_1]^{(2)} || I_1)$$

in terms of a 6- j coefficient and the reduced matrix element of $[I_1]^{(2)}$, namely

$$[33] \quad (I_1 || [I_1]^{(2)} || I_1) = (1/6)I_1(I_1+1)(2I_1-1)(2I_1+3)(2I_1+1)$$

Note that the term $(1 + (-1)^{I+I'})$ restricts I and I' to be either even or odd but not mixed even

and odd. This naturally accounts for the spin symmetry requirements on I and I' . By summing [32] over I' and using orthogonality relations for $6-j$'s, [31] is obtained.

The various contributions to relaxation can now be given. From [5], [32], and [29] the contributions from each fixed I and also transitions between I 's can be calculated. The expression for the former case is

$$[34] \quad \left(\frac{1}{T_1}\right)_{II} = \frac{3}{200} \left(\frac{eqQ}{\hbar}\right)^2 \sum_J \bar{p}_J \left(\frac{J(J+1)}{(2J-1)(2J+3)}\right) \left(\frac{(2I-1)(2I+3)}{I_1^2(2I_1-1)^2}\right) \\ \times (2I+1) \left[1 - \frac{4I_1(I_1+1) + I(I+1)}{(2I-1)(2I+3)}\right]^2 \left[\frac{\tau}{1 + (\omega_{I_1} - \omega_J)^2 \tau^2} + \frac{4\tau}{1 + 4(\omega_{I_1} - \omega_J)^2 \tau^2}\right]$$

while the $(1/T_1)_{II'}$ term follows from substitution of [32] into [29] without the II' sum. Actually the total expression for relaxation of a species can be given in a more concise form than [5]. As noted above, the I' sum can be performed to give [31], which can be substituted into [29] for the "1" contribution of $(1 + \delta_{I',0})$. The contribution arising from $\delta_{I',0}$ can be calculated from

$$[35] \quad \gamma(I,0,I_1) = (2/15)(2I+1)I_1(I_1+1)(2I_1-1)(2I_1+3)(2I_1+1)\delta_{I,2}$$

and can be included in [29]. The final expression is

$$[36] \quad \left(\frac{1}{T_1}\right)_s = \frac{3}{100} \left(\frac{eqQ}{\hbar}\right)^2 \sum_{I,T=0}^{2I_1} \bar{p}_J \left(\frac{J(J+1)}{(2J-1)(2J+3)}\right) \left(\frac{(I_1+1)(2I_1+3)}{I(I+1)I_1(2I_1-1)}\right) \\ \times (2I+1) \left[1 + \frac{(3/4 C_I(C_I+1) - I_1^2(I_1+1)^2)}{I_1(I_1+1)(2I_1-1)(2I_1+3)}\right] + \frac{2}{5} \delta_{I,2} \\ \times \left[\frac{\tau}{1 + (\omega_{I_1} - \omega_J)^2 \tau^2} + \frac{4\tau}{1 + 4(\omega_{I_1} - \omega_J)^2 \tau^2}\right]$$

IV. Discussion

The partition function [26] contains the spin degeneracies for a given species. The I sum can be performed for I odd or even so that the fraction of ortho or para molecules with spin I actually is treated. In calculating the coefficients for particular values of I_1 , the spin degeneracy is removed from the partition function,

$$[37] \quad \bar{p}_J = p_J \sum_{I=0}^{2I_1} (2I+1)$$

and included in the coefficient of $(1/T_1)_s$. Equation 36 can be written as

$$[38] \quad (1/T_1)_s = \mathcal{G}(I_1)(eqQ/\hbar)^2 [j_3(\omega_{I_1} - \omega_J) + 4j_3(2(\omega_{I_1} - \omega_J))]$$

where, to conform with popular notation, $j_s(\mu\omega)$ has been defined as

$$[39] \quad j_s(\mu\omega) \equiv \sum_J p_J \frac{J(J+1)}{(2J+1)(2J+3)} \frac{2\tau}{1 + \mu^2 \omega^2 \tau^2}$$

as well as

$$[40] \quad \mathcal{G}(I_1) = \frac{3}{200} \left(\frac{(I_1+1)(2I_1+3)}{I_1(2I_1-1) \sum_{I=0}^{2I_1} (2I+1)}\right) \sum_{I=0}^{2I_1} \frac{(2I+1)}{I(I+1)} \\ \times \left[1 + 2 \left(\frac{3/4 C_I(C_I+1) - I_1^2(I_1+1)^2}{I_1(I_1+1)(2I_1-1)(2I_1+3)}\right) + \frac{2}{5} \delta_{I,2}\right]$$

TABLE 1. The numerical values of $\mathcal{G}(I_1)$ summed over odd and even I for various values of I_1 and their ratio, evaluated by machine. The values in the brackets are not multiplied by 10^3

Spin I_1	$\mathcal{G}(I_1) \times 10^3$		Ratio odd/even
	Odd I sum	Even I sum	
1	(3/80) 37.500	(3/80) 37.500	1.000
3/2	(3/160) 18.750	(1/100) 10.000	1.875
2	13.125	5.875	2.234
5/2	6.650	4.425	1.502
3	5.700	2.792	2.042
7/2	3.475	2.455	1.416
4	3.186	1.697	1.878
9/2	2.165	1.574	1.375
5	2.047	1.160	1.764
11/2	1.491	1.104	1.350

Table 1 gives the values of $\mathcal{G}(I_1)$ for special cases of I_1 evaluated by machine. The two middle columns give the coefficients for the odd and even I sum respectively, and the last gives the ratio of odd to even. As can be seen, the ratio is 1 only in the case of $I_1 = 1$ in agreement with Bloom (1973). Hence it is expected that a two-relaxation process should be observed in nuclear spin relaxation studies of homonuclear diatomics of nuclear spin greater than 1, even at temperatures where the odd and even J averages are about equal.

By use of [34] and [29], it is possible to calculate the contribution to relaxation from individual I levels and from transitions between I states. For example with $I_1 = 1$, 11/15 of the ortho relaxation arises from the $I = 2$ state while transitions between $I = 2 \leftrightarrow 0$ account for the remaining 4/15. It is also interesting to note that for the para species with $I_1 = 3/2$, relaxation can occur only through transitions between states with $I = 2$ and states with $I = 0$. The $I = 2 \leftrightarrow 2$ term vanishes as can be seen from [34]. In all cases, for a given I_1 , in both ortho and para species, the individual contributions decrease with increasing I .

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