

Nuclear spin relaxation by intramolecular interactions in gases of homonuclear diatomic molecules¹

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The differential equations which describe the relaxation of macroscopic observables associated with nuclear spins in homonuclear diatomic molecules are derived using an expansion of the nuclear spin density matrix in terms of irreducible tensors. It is shown, using an *intramolecular* quadrupole mechanism, that the only difference between nuclear spin relaxation of the ortho- and para-species arises from the rotational states being restricted to odd and even values. This difference is vanishingly small at high temperatures so that the relaxation equations for nuclear magnetization become identical for both species. A previous paper predicting a difference even at high temperatures is shown to be in error and is corrected.

On obtient les équations différentielles qui décrivent la relaxation des observables macroscopiques associés aux spins nucléaires dans les molécules diatomiques homonucléaires en utilisant un développement de la matrice densité des spins nucléaires en termes de tenseurs irréductibles. On montre en utilisant un mécanisme de quadrupole *intramoléculaire*, que la seule différence entre les espèces ortho et para, pour ce qui est de la relaxation de spin nucléaire, provient de la restriction imposée aux états de rotation d'être impairs ou pairs. Cette différence tend à disparaître aux températures élevées, de sorte que les équations de relaxation pour l'aimantation nucléaire deviennent les mêmes pour les deux espèces. On montre qu'il y avait une erreur dans un article antérieur qui prédisait une différence même aux températures élevées et on corrige cette erreur.

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In an earlier paper by one of us (Sanctuary 1973), the nuclear spin relaxation time T_1 was derived for the ortho- and para-species of a homonuclear diatomic molecule. Using an *intramolecular* quadrupole interaction, it was found that the two species relax at different rates for $I > 1$ even at temperatures high enough that averages of molecular quantities over the odd and even rotational states are approximately equal. The purpose of this paper is to show that this result is incorrect, that the relaxation, in general, is not exponential and that the relaxation equations for the two nuclear spin symmetry species are identical to each other at high temperatures. In fact, for *intramolecular* quad-

rular interactions we show that the relaxation equations for the magnetization of the ortho- and para-species are identical to each other and completely equivalent to those of two uncorrelated nuclear spins. Thus the only role played by the identical spins is via averages of molecular quantities over the rotational states of the two species.

The *intramolecular* quadrupolar Hamiltonian \mathcal{H}_Q for a diatomic molecule is given by (Abragam (1961), p. 233)

$$[1] \quad \mathcal{H}_Q = K \sum_{q=-2}^{+2} A_{2q} Y_{2q}^*(\theta, \phi)$$

where

$$[2] \quad K = \frac{\sqrt{\pi}}{10} e q Q \left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)} \right]^{1/2}$$

and

$$[3] \quad A_{2q} = \hat{T}_{2q}(I_1) L_2 + E_1 \hat{T}_{2q}(I_2)$$

$Y_{2q}(\theta, \phi)$ is a spherical harmonic of the angles θ , ϕ associated with the vector joining the two nuclei and $I = I_1 = I_2$ is the spin of each nu-

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cleus. The quadrupolar coupling constant is eqQ and F_i is the identity operator for the spin degrees of freedom of nucleus i . Finally, $\hat{T}_{2q}(I_i)$ is the q th spherical component of the normalized irreducible tensor of rank 2 associated with the spin I_i of nucleus i . It is given explicitly by

$$[4] \quad \hat{T}_{2q}(I_i) = \frac{\sqrt{30}T_{2q}(I_i)}{[I(I+1)(2I+3)(2I+1)(2I-1)]^{1/2}}$$

where $T_{2q}(I_i)$ is the unnormalized spherical tensor components defined by, e.g., Rose (1957) and Tinkham (1964). Explicitly, $T_{20}(I) = (6)^{-1/2}(3I^2 - I(I+1))$. The normalization is chosen such that

$$[5] \quad \text{Tr} \{ \hat{T}_{LM} \hat{T}_{L'M'}^\dagger \} = \delta_{LL'} \delta_{MM'}$$

In general, the \hat{T}_{LM} 's are found to be (Sanctuary 1976; Coope and Snider 1972)

$$[6] \quad \hat{T}_{LM}(I) = \left[\frac{(2L+1)2^L(2L)!(2I-L)!}{(L!)^2(2I+L+1)!} \right]^{1/2} T_{LM}(I_i)$$

In the gas phase, nuclear spin relaxation is caused by molecular collisions which reorient the molecule thereby causing the rotational angular momentum J to change direction, or, equivalently, producing transitions between rotational m_j states. The effect of collision-induced molecular reorientation is to cause the angles θ, ϕ in [1] to be time dependent; thus inducing nuclear spin transitions via the spin-dependent interaction \mathcal{H}_Q (Bloom 1972; Abragam 1961).

The relaxation equation for the spin density matrix $\hat{\sigma}$ in a co-ordinate system rotating about the applied magnetic field at the nuclear spin Larmor frequency ω_0 has been derived using time dependent perturbation theory to be (Abragam (1961), equation (42), p. 279)

$$[7] \quad \frac{d\hat{\sigma}}{dt} = -\frac{K^2}{2\hbar^2} \sum_{q=-2}^{+2} J_q(\omega_0) [A_{2q}^\dagger, [A_{2q}, \hat{\sigma}]]$$

where $J_q(\omega)$ is the spectral density of the correlation function of $Y_{2q}(\theta, \phi)$.

It is convenient for our purposes to expand σ , the density matrix in the laboratory frame, in terms of the tensors $\hat{T}_{LM}(I_i)$ for each nucleus

$$[8] \quad \sigma(t) = \sum_{L, L'=0}^{2I} \sum_{M=-L}^{+L} \sum_{M'=-L'}^{-L'} \times a_{MM'}^{LL'}(t) \hat{T}_{LM}(I_1) \hat{T}_{L'M'}(I_2)$$

The products $\hat{T}_{LM}(I_1) \hat{T}_{L'M'}(I_2)$ form a complete set in the $(2I_1+1)(2I_2+1)$ dimensional nuclear spin space of the diatomic molecule. The representation of the density matrix in terms of products of irreducible tensors is commonly used in relaxation problems in atomic physics (Happer 1972) and in the kinetic theory of polyatomic gases (Ferziger and Kaper 1972). From the orthonormal properties of the irreducible spherical tensors, it may be seen that a macroscopic observable $\langle Q \rangle$ associated with a quantum mechanical operator $Q = \hat{T}_{lm}(I_1) \hat{T}_{l'm'}(I_2)$ has a value

$$[9] \quad \langle Q \rangle = \text{Tr}(Q\sigma) = a_{mm'}^{ll'}(t) = \tilde{a}_{mm'}^{ll'}(t) e^{i(m+m')\omega_0 t}$$

We separate σ into three sets of terms

$$[10] \quad \sigma = \sigma_0 + \sigma_s + \sigma_c$$

The *first term* is just the product of the two identity operators $\sigma_0 = E_1 E_2$, i.e. $L = L' = 0$. The *second term* is a 'single spin term' associated with the values of the indices $L = 0, L' \neq 0$ and $L \neq 0, L' = 0$. The coefficient $a_{M'0}^{L0}$ and a_{0M}^{0L} , therefore, represent macroscopic quantities involving single spin quantities. In fact, the term $a_{M'0}^{L0}$ involves *only* observables associated with I_1 and a_{0M}^{0L} *only* those of I_2 so that the spin density matrix terms associated with them may be denoted by $\sigma_{s1}(t)$ and $\sigma_{s2}(t)$ respectively, with no ambiguity. The *third term* involves products of irreducible tensors in which both L and L' are non-zero. Their coefficients $a_{MM'}^{LL'}$ are associated with macroscopic observables which depend on correlations between the two spins.

Since all $\hat{T}_{L'M'}(I_i)$ commute with all $\hat{T}_{LM}(I_j)$ for $i \neq j$, and since E_i commutes with all $\hat{T}_{LM}(I_j)$ for all i, j , it is clear that

$$[11] \quad [\sigma_{s1}, E_1 \hat{T}_{LM}(I_2)] = [\sigma_{s2}, \hat{T}_{LM}(I_1) E_2] = 0$$

for any LM . In addition, $[\sigma_{s1}, \hat{T}_{LM}(I_1) E_2]$ involves only operators of the type $\hat{T}_{L'M'}(I_1) E_2$.

Substituting [3] and [8] into [7] and using [9], [10], and [11], it follows that

$$[12] \quad \frac{d}{dt} \tilde{a}_{M'0}^{L0} = - \sum_{L''M''} b_{LL''MM''} \tilde{a}_{M''0}^{L''0}(t)$$

where the coefficients

$$[13] \quad b_{LL'MM'} = \frac{K^2}{2\hbar^2} \sum_{q=-2}^{+2} J_q(q\omega_0) \text{Tr} \{ [\hat{T}_{LM}(I), \hat{T}_{2q}(I)] [\hat{T}_{2q}(I), \hat{T}_{L'M'}(I)] \}$$

are identical to those obtained in the corresponding differential equation for $\hat{a}_{OM}^{(I)}(t)$. Thus the relaxation equations obtained for σ_{s1} and σ_{s2} are identical with each other and to their sum $\sigma_s = \sigma_{s1} + \sigma_{s2}$. It follows that the relaxation equations for nuclear magnetization for the two-spin molecule are formally equivalent for quadrupolar relaxation to those of a single spin. The only difference between the relaxation rates of macroscopic observables represented by operators of the form $Q = \hat{T}_{lm}(I_1)E_2 + E_1\hat{T}_{lm}(I_2)$, such as magnetization ($l = 1$), for the ortho- and para-species arises from averages over the different rotational states of the two species of the molecular parameters arising from the terms in $J_q(q\omega_0)$ in [7]. These differences become vanishingly small at high temperatures.

The commutators in [13] can be explicitly calculated (see, e.g., Sanctuary (1976), equation (46); Rose (1962); Ambler *et al.* (1962)) and the resulting expression written in terms of 3- j and 6- j coefficients (Edmond 1961).

$$[14] \quad b_{LL'MM'} = \delta_{MM'} \frac{\pi}{10} \left(\frac{eqQ}{\hbar} \right)^2 \left[\frac{(I+1)(2I+1)(2I+3)}{I(2I-1)} \right] \sum_{\lambda=0}^{2I} \phi(\lambda, 2L) \phi(\lambda, 2L') (2\lambda+1) \\ \times \begin{Bmatrix} I & 2 & \lambda \\ I & I & I \end{Bmatrix} \begin{Bmatrix} L' & 2 & \lambda \\ L' & L' & L' \end{Bmatrix} \sum_{q=-2}^2 J_q(q\omega_0) [(2L+1)(2L'+1)]^{1/2} \\ \times \begin{pmatrix} L & 2 & \lambda \\ -M & q & M-q \end{pmatrix} \begin{pmatrix} L' & 2 & \lambda \\ -M & q & M-q \end{pmatrix}$$

The quantity $\phi(l_1, l_2, l_3)$ is equal to unity if the sum $l_1 + l_2 + l_3$ is odd and zero otherwise. Hence L and L' are either *both* even or *both* odd. Moreover the $b_{LL'MM'}$'s obey the symmetry relation

$$[15] \quad b_{LL'MM'} = b_{L'LMM}$$

For $l = 1$, the relaxation of the magnetization ($L = 1$) is exponential since only $L' = 1$ contributes to [14]. In this case $1/T_1$ is given by b_{1100} with $I = 1$, $\lambda = 2$. It is easily shown that this form agrees with Abragam (1961, equation (138), p. 314). For $l = 3/2$ and 2, $L = 1$ and 3 contribute to the nuclear spin relaxation giving rise to a sum of two exponentials. Spins of 5/2 and greater involve coupling to multiples of rank $L' = 5$ and higher and are generally nonexponential. On the other hand, as shown by Pyper (1971), in the extreme narrowing limit, the q dependence of $J_q(q\omega_0)$ can be neglected resulting in exponential decay for spins of any magnitude. This is seen from the orthogonality of the 3- j 's in [14] giving $L = L'$. In this case $1/T_1$ is given by b_{1100} with $\lambda = 2$ for *any* I and agrees with the expression given by Abragam ((1961), equation (137), p. 314).

In a previous paper (Sanctuary 1973), the problem of nuclear spin relaxation in ortho- and para-species was treated by evaluating the relaxation tensor for the s -th species $(I/T)_s$ (equation (19) of Sanctuary (1973)). This procedure assumes that the Bloch equations are obeyed from the outset and focuses attention on the different spin weightings due to ortho-para restrictions. It was found, in contradiction to the calculation here, that the ortho- and para-species have different relaxation times even at high temperatures. This conclusion was obtained due to an error in normalization in [22] of Sanctuary (1973). The correct result is

$$[16] \quad \langle P_s I \cdot P_s I \rangle = 2 \sum_{I'} (1 + (-1)^{I+I'}) (2I+1)(2I'+1) \begin{Bmatrix} I & I & I' \\ I_1 & I_1 & I_1 \end{Bmatrix}^2 \langle I_1 || I_1 || I_1 \rangle^2$$

where I, I' are the total spin magnitudes of the resultant $I = I_1 + I_2$ with values that range from 0 to $2I_1$. The prime on the summation restricts these to either odd or even integers as symmetry requires. Carrying the expression [16] through the calculation subsequent to [22] in Sanctuary (1973) gives the result $1/T_1 = b_{1100}$ in agreement with the expression developed in this paper.

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