

On the Theory of Spin Relaxation of Gas Molecules: The Strong-Collision Limit

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A model of spin relaxation of gas molecules based upon an assumption of strong collisions is developed. A relaxation matrix formally similar to that of Redfield, but with different spectral densities, is obtained. The nuclear magnetic relaxation of gaseous orthohydrogen is discussed in terms of these results, and it is shown that, in general, molecules in different J states are expected to exhibit different relaxation times (a conclusion that is independent of the strong collision assumption) whenever the collision mechanism is effective only in reorienting J but not in changing its magnitude. Otherwise statistical averages of relaxation times are obtained. Relaxation of more complex molecules is also discussed.

1. INTRODUCTION

IN this note we derive an expression for the nuclear or electronic spin relaxation of gas-phase molecules based on a model for the "strong-collision" limit. The model represents a generalization of the Schwinger-Bloembergen (SB)¹ theory for orthohydrogen in the $J=1$ state, and retains some of its simplifying features.

There have been a number of experimental studies on the relaxation of orthohydrogen, which have been analyzed primarily in terms of the SB approach.¹⁻⁴ A result of this work has been a renewed interest in extending the theoretical framework of gas phase relaxation. Needler and Opechowski (NO)⁵ have presented a generalization of the SB theory to calculate the longitudinal relaxation time T_1 for orthohydrogen when higher J states are excited, but the generality of their work was limited by a number of approximations most significant of which were their neglect of off-diagonal elements in the density matrix and their dependence on the spin temperature concept. (From a practical point of view both these assumptions preclude the possibility of calculating transverse relaxation times T_2 from the theory because they essentially require $T_2 \approx 0$.) Furthermore, it was not clear what physical justification there was for the way they introduced exponentially decaying correlation functions. Recently Bloom and Oppenheim (BO)^{6,7} have presented a theory for orthohydrogen in the $J=1$ state relating T_1 and T_2 to detailed intermolecular forces. They also have made some predictions which follow from the NO theory, on the inclusion of higher J states.⁷ Their theory is pri-

marily a "weak-collision" one, i.e., the rotational transition probabilities per collision are assumed to be small.

Some experimental NMR studies have recently been performed on more complex gas molecules, such as methane, ethane, and ethylene,^{8,9} and there is considerable interest in the ESR of gaseous, polyatomic free radicals.¹⁰ The present work was undertaken to obtain a theoretical formulation which could be used for studying the spin relaxation of such gaseous molecules. It was also deemed useful to reformulate a model which could clarify some of the relevant physical assumptions, and the results for orthohydrogen, when more than one J state is appreciably populated, are compared to the NO and BO theories.

The analysis in this work is simplified by the assumption of "strong collisions" because it is then unnecessary to consider the collision process in detail. Some limitations are thereby placed on the applicability of the resulting theory, although this assumption can be modified somewhat. There is, however, some evidence that a strong-collision approximation would be more appropriate for larger molecules.⁸

The theoretical formulation is given in Sec. 2. In Sec. 3 the relaxation of orthohydrogen is discussed, and the relaxation of more complex molecules is briefly discussed in Sec. 4.

2. THEORY

Let $\hbar H$ represent the Hamiltonian for a gaseous paramagnetic molecule in a magnetic field. If it is assumed that the spin and rotational states are independent of the other degrees of freedom of the molecule, then we may write

$$\hbar H = \hbar H_r + \hbar H_s' + \hbar V', \quad (2.1)$$

⁸ M. Bloom, M. Lipsicas, and B. H. Muller, *Can. J. Phys.* **39**, 1093 (1961).

⁹ C. S. Johnson, Jr., and J. S. Waugh, *J. Chem. Phys.* **35**, 2020 (1961).

¹⁰ M. Karplus, *J. Chem. Phys.* **30**, 15 (1959); R. J. Myers in "Symposium on Spectroscopy of Free Radicals," American Chemical Society, 133rd National Meeting, April, 1958; J. C. Baird, Jr., and G. R. Bird, *Bull. Am. Phys. Soc.* **4**, 68 (1959).

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¹ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

² M. Bloom, *Physica* **23**, 237, 378 (1957).

³ M. Lipsicas and M. Bloom, *Can. J. Phys.* **39**, 881 (1961).

⁴ C. S. Johnson, Jr., and J. S. Waugh, *J. Chem. Phys.* **36**, 2266 (1962).

⁵ G. T. Needler and W. Opechowski, *Can. J. Phys.* **39**, 870 (1961).

⁶ I. Oppenheim and M. Bloom, *Can. J. Phys.* **39**, 845 (1961).

⁷ M. Bloom and I. Oppenheim, *Can. J. Phys.* **41**, 1580 (1963)

where $\hbar H_r$ and $\hbar H_s'$ are the unperturbed Hamiltonians of the rotational and spin systems, respectively, while V' is the coupling term operating on both rotational and spin variables, and H is time-independent. Since ensembles of molecules are of interest, the density matrix ρ , which obeys the equation

$$(1/i)(d\rho/dt) = -[H, \rho(t)], \quad (2.2)$$

is introduced. It is convenient to introduce the definitions:

$$H_s = H_s' + \langle V' \rangle, \quad (2.3a)$$

$$V = V' - \langle V' \rangle, \quad (2.3b)$$

where

$$\langle V' \rangle = \text{Tr}_r \{ B(r) V' \}, \quad (2.3c)$$

$B(r)$ is the Boltzmann distribution in rotational states,

$$B(r) = Z(r) \exp(-\hbar H_r / KT);$$

$$Z(r)^{-1} = \text{Tr}_r \{ \exp(-\hbar H_r / KT) \}, \quad (2.3d)$$

and Tr_r represents a trace over rotational states.

In the interaction representation with

$$\rho^*(t) = \exp[i(H_r + H_s)t] \rho(t) \exp[-i(H_r + H_s)t], \quad (2.4a)$$

and

$$V^*(t) = \exp[i(H_r + H_s)t] V \exp[-i(H_r + H_s)t], \quad (2.4b)$$

one has

$$(1/i)[d\rho^*(t)/dt] = -[V^*(t), \rho^*(t)]. \quad (2.5)$$

Equation (2.5) may be solved by integrating to successive approximations¹¹ obtaining a series of expansion for the dependence of $\rho^*(t)$ on its value at some earlier time $\rho^*(t_0)$.

To proceed further, the following assumptions are introduced.

(1) $\rho(t)$ is factorable into the product $\lambda(t)\sigma(t)$, where $\lambda(t)$ and $\sigma(t)$ are reduced density matrices depending only on the rotational and spin degrees of freedom, respectively. [This is a weaker assumption than the frequently used one that the lattice always remains at equilibrium,¹¹⁻¹⁴ i.e., $\rho(t) = B(r)\sigma(t)$, which is not strictly correct in the present case, since the rotational degrees of freedom would not always be expected to be a large thermal reservoir compared to the heat capacity of the spin systems.]

(2) Collisions affect only the rotational degrees of freedom (i.e., they are perturbations with no matrix elements between spin states).

(3) The collision takes place over an interval of time which is short enough that $\sigma(t)$ remains essentially constant.

(4) The collision is strong in the sense that the distribution of rotational states just after collision is given by a Boltzmann distribution at the kinetic temperature of the molecules and is independent of their distribution just before collision,¹⁵ so that

$$\rho(t_0) = B(r)\sigma(t_0). \quad (2.6)$$

[Any phase coherence between rotational states which may be induced by the collision process is either neglected or the collision interval in Assumption (3) is taken to include the time for the phase coherence to become small.] In order to be consistent with Assumption (2), collisions must not change the spin symmetry. Thus, the symmetry of the rotational states will be unchanged and $B(r)$ will be understood as normalized only over states r having the symmetry of interest. Some of the limitations on the model, that are introduced by Assumption (4) can be removed and the pertinent modifications are discussed in Sec. 3. However, collisional selection rules of the type suggested by Johnson and Waugh⁴ may not be readily included into the present formulation.

(5) The collisions are random with a mean time interval τ . The simple, hard-sphere kinetic-theory collision time is given by¹⁶

$$\tau_c^{-1} = 4a^2 D (\pi K T / m)^{1/2},$$

where a is the diameter of the molecule, m its mass and D is the number of molecules per cubic centimeter. The possibility that not all hard-sphere collisions will be effective in the sense of Assumption (4) is allowed for by using an effective collision time $\tau \geq \tau_c$.

It should be noted that a reduced spin-density matrix may always be obtained as $\sigma(t) = \text{Tr}_r \rho(t)$.¹¹ Thus, while Assumption (1) is not needed in order to have a well defined $\sigma(t)$, and does not, in itself, affect the final results, it leads to a more obvious acceptance of the other assumptions. Assumption (1) appears quite reasonable if one only looks at $\rho^*(t)$ for times $\theta = t - t_0$ [where Eq. (2.6) is held at time t_0] short enough that the perturbation V has had a very small effect on $\rho^*(t)$. This is essentially the condition for validity of the expansion of $\rho(t)$ to second order in V which is utilized below. Thus in this model, collisions represent a very strong perturbation which rapidly restores the rotational states to equilibrium, while the spin-rotational interaction is a much weaker perturbation that slowly tends to bring the spins to equilibrium.

¹⁵ Some of the implications of such an approximation are discussed by J. H. Van Vleck and V. F. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945). In the present case this assumption also implies that collisions rerandomize the phases of the rotational states, so density matrix elements off-diagonal with respect to rotational states are made to vanish.

¹⁶ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

¹¹ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. 8.

¹² A. G. Redfield, *IBM J. Res. Develop.* **1**, 19 (1957).

¹³ P. S. Hubbard, *Rev. Mod. Phys.* **33**, 249 (1961).

¹⁴ F. Bloch, *Phys. Rev.* **102**, 104 (1956).

Assuming that a collision occurred at t_0 , expanding Eq. (2.5) to second order, and taking Tr_r now gives:

$$\begin{aligned} [\partial\sigma^*(t, t_0)/\partial t] = & -i \text{Tr}_r\{[V^*(t), B(r)\sigma^*(t_0)]\} \\ & - \text{Tr}_r\left(\int_{t_0}^t dt' [V^*(t), [V^*(t'), B(r)\sigma^*(t_0)]]\right) + \dots, \end{aligned} \quad (2.7)$$

where $\sigma^*(t, t_0) = \text{Tr}_r \rho^*(t, t_0)$ is the spin-density matrix at time t and is expressed in terms of its value at the time of collision. It is usually possible to express

$$V' = \sum_q K^{(q)} F^{(q)}, \quad (2.8)$$

where $K^{(q)}$ is a spin operator and $F^{(q)}$ a rotation operator. Then:

$$V^*(t) = \sum_q [F^{(q)*}(t) - \langle F^{(q)} \rangle] K^{(q)*}(t), \quad (2.9a)$$

where

$$\langle V' \rangle = \sum_q K^{(q)} \langle F^{(q)} \rangle, \quad (2.9b)$$

$$F^{(q)*}(t) = \exp(iH_r t) F^{(q)} \exp(-iH_r t), \quad (2.9c)$$

$$K^{(q)*}(t) = \exp(iH_s t) K^{(q)} \exp(-iH_s t). \quad (2.9d)$$

When V' does not connect states of different spin symmetry, and any change of spin symmetry resulting from collisions is neglected, then all molecules of a particular spin symmetry may be treated as a separate subensemble represented by a separate Eq. (2.7). It follows readily from Eqs. (2.9) that the first term on the left of Eq. (2.7) vanishes.

To obtain $\sigma^*(t)$ from Eq. (2.7), $\sigma^*(t, t_0)$ must be integrated over all values of $t_0 = t - \theta$. From Assumption (5) the probability that the last collision occurred during the interval, $t - \theta, t - \theta - d\theta$ is $\tau^{-1} e^{-\theta/\tau} d\theta$. Thus

$$\sigma^*(t) = \int_0^\infty \sigma^*(t, t - \theta) \tau^{-1} e^{-\theta/\tau} d\theta. \quad (2.10)$$

Differentiating partially with respect to time gives

$$\begin{aligned} \frac{\partial}{\partial t} \sigma^*(t) = & \int_0^\infty \left[\frac{\partial}{\partial t} \sigma^*(t, t_0) \right]_{t_0=t-\theta} \tau^{-1} e^{-\theta/\tau} d\theta \\ & - \int_0^\infty \frac{\partial}{\partial \theta} \sigma^*(t, t - \theta) \tau^{-1} e^{-\theta/\tau} d\theta. \end{aligned} \quad (2.11)$$

The term $[(\partial/\partial t) \sigma^*(t, t_0)]_{t_0=t-\theta}$ in Eq. (2.11) is just that given by Eq. (2.7). The second term in Eq. (2.11) is shown to be zero by first integrating it by parts giving $\tau^{-1} [\sigma^*(t) - \sigma^*(t, t_0 = t)]$ and then by utilizing Assumptions (3) and (5), which permit Eq. (2.10) to be written where $\sigma^*(t)$ on the lhs is replaced by $\sigma^*(t, t_0 = t)$, and $t - \theta$ on the rhs is the time of the collision previous to the one at $t = t_0$. This leaves the follow-

ing expression:

$$\begin{aligned} \frac{\partial \sigma^*(t)}{\partial t} = & - \text{Tr}_r \int_0^\infty \tau^{-1} e^{-\theta/\tau} d\theta \\ & \times \int_0^\theta dx [V^*(t), [V^*(t-x), B(r)\sigma^*(t-\theta)]] + \dots, \end{aligned} \quad (2.12)$$

where the substitution $x = t - t'$ has been employed. Equation (2.12) may be solved using the approximations: (a) Replace $\sigma^*(t - \theta)$ on the right by $\sigma^*(t)$, and (b) neglect higher-order terms in the expansion. These approximations are very similar to the ones introduced into the semiclassical theories of relaxation¹¹⁻¹⁴ and the condition for their validity in the present case may be shown to be very similar. It may be written as $V^2 \ll \tau^{-2}$ which will lead to $T_1, T_2 \gg \tau$, i.e., the relaxation effects of the perturbation V are much weaker than those of the collisions. This approximation has already been found useful in connection with Assumption (1).

Equation (2.12) is evaluated in a basis diagonal in H_r and H_s . That is, if ψ_r and φ_s are, respectively, complete sets of eigenfunctions of H_r and H_s having the correct symmetry for the spin species of interest, then the appropriate basis would be the set of products $\psi_r \varphi_s$. Each of the four terms arising out of the expansion of the double commutators in Eq. (2.12) is treated separately. The procedure is outlined in Appendix I. The final results neglecting the second-order frequency shifts (see Appendix I) are:

$$\partial \sigma^*(t)_{\alpha\alpha'}/\partial t = \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \sigma^*(t)_{\beta\beta'}, \quad (2.13)$$

where

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'} = & \sum_{q, q'} [K_{\alpha\beta}^{(q)} K_{\beta'\alpha'}^{(q')} 2j_{qq'}(\alpha - \beta) \\ & - \sum_\gamma \delta_{\alpha\beta} K_{\beta'\gamma}^{(q')} K_{\gamma\alpha'}^{(q)} j_{qq'}(\gamma - \beta') \\ & - \sum_\gamma \delta_{\alpha'\beta'} K_{\alpha\gamma}^{(q')} K_{\gamma\beta}^{(q)} j_{qq'}(\gamma - \beta)]. \end{aligned} \quad (2.14)$$

Equation (2.14) is formally very similar to Redfield's Eq. (3.13)¹² (there are some differences in the last two terms) but the spectral densities $j(\alpha - \beta)$ are different:

$$\begin{aligned} j_{qq'}(\alpha - \beta) = & Z(r) \\ & \times \sum_{r, r'} \left[\exp(-E_{rr'}/KT) F_{rr'}^{(q)} F_{r'r}^{(q')} \frac{\tau}{1 + (\omega_{rr'} + \omega_{\alpha\beta})^2 \tau^2} \right] \\ & - \langle F^{(q)} \rangle \langle F^{(q')} \rangle \frac{\tau}{1 + \omega_{\alpha\beta}^2 \tau^2}, \end{aligned} \quad (2.15)$$

where $\hbar\omega_{rr'} = E_r - E_{r'}$, etc. Equations (2.13) and (2.14) require the energy restriction that $E_\alpha - E_\beta = E_{\alpha'} - E_{\beta'}$.

As is often done^{11,12} the *ad hoc* assumption that $\sigma^*(t)$ relaxes to

$$\begin{aligned} \sigma^T = & Z(s) \exp(-\hbar H_s/KT); \\ Z(s)^{-1} = & \text{Tr}_s \{ \exp(-\hbar H_s/KT) \}, \end{aligned}$$

TABLE I. Terms in the perturbation V' for orthohydrogen.

$V' = \sum_q F^{(q)} K^{(q)}$	$q = -4 \dots 0 \dots +4$
$\delta^{-1} F^{(0)} = J_z$	$K^{(0)} = I_z$
$\delta^{-1} F^{(\pm 1)} = \frac{1}{2} J_{\mp}$	$K^{(\pm 1)} = I_{\pm}$
$\epsilon^{-1} F^{(\pm 2)} = 3 J_z^2 - J^2$	$K^{(\pm 2)} = \frac{2}{3} (2 I_{1z} I_{2z} - (\frac{1}{2}) I_{1\pm} I_{2\mp})$
$\epsilon^{-1} F^{(\pm 3)} = J_z J_{\mp} + J_{\mp} J_z$	$K^{(\pm 3)} = I_{1z} I_{2\pm} + I_{1\pm} I_{2z}$
$\epsilon^{-1} F^{(\pm 4)} = J_{\mp}^2$	$K^{(\pm 4)} = I_{1\pm} I_{2\pm}$
$\delta = \gamma H'$	
$\epsilon = 3\gamma H'' / (2J-1)(2J+3)$	

is introduced by replacing $\sigma^*(t)$ with $\sigma^*(t) - \sigma^T$ in Eq. (2.13).¹⁷ The macroscopic observable $m(t)$ of an operator M may be calculated after transforming Eq. (2.13) back to the Schrödinger representation and using $m(t) = \text{Tr}\{\sigma(t)M\}$. If only the effect of the perturbation V upon $m(t)$ is of interest, use can be made of $m^*(t) = \text{Tr}\{\sigma^*(t)M\}$ obtaining

$$\frac{dm^*(t)}{dt} = \sum_{\substack{\alpha, \alpha' \\ \beta, \beta'}} R_{\alpha\alpha', \beta\beta'} (\sigma^* - \sigma^T)_{\beta\beta'} M_{\alpha'\alpha}. \quad (2.16)$$

It is worthwhile to note that the results of calculations of $m^*(t)$ using a semiclassical theory¹¹ can sometimes apply to the present case provided that the spectral-density Eq. (2.15) is employed.

3. APPLICATION TO ORTHOHYDROGEN

The magnetic relaxation of gaseous orthohydrogen is perhaps the simplest case for the application of the general formulation given in Sec. 2 and is indicative of the way that more complex molecules may be handled. There is reasonable evidence that weak collisions are occurring in the hydrogen system^{2,3} and this consideration is treated very crudely by letting $\tau < \tau_c$ in Assumption (5) of Sec. 2. The terms in the Hamiltonian, Eq. (2.1) are for this case¹¹

$$H_r = C J^2 + \omega_J J_z, \quad (3.1)$$

$$H_s' = \omega_I I_z, \quad (3.2)$$

and

$$V' = \gamma H' \mathbf{I} \cdot \mathbf{J} + \gamma H'' [\mathbf{I}_1 \cdot \mathbf{I}_2 - 3(\mathbf{I}_1 \cdot \mathbf{n})(\mathbf{I}_2 \cdot \mathbf{n})], \quad (3.3)$$

where $\hbar C J^2$ is the rotational energy of the molecule, \mathbf{I}_1 and \mathbf{I}_2 are the spins of the two protons with $\mathbf{I}_1 + \mathbf{I}_2 = \mathbf{I}$, $\omega_I = -\gamma H_0$ is the proton Larmor frequency in the applied field H_0 , ω_J is the Larmor frequency of \mathbf{J} , $H' = 27$ G is the spin-rotation coupling constant, $H'' = 34$ G is the dipolar coupling constant between

the two protons, d is their distance, and \mathbf{n} is the unit vector \mathbf{d}/d .

The eigenfunctions ψ_r are the spherical harmonics of odd J values with energies: $\hbar C J(J+1) + \hbar \omega_J J_z$, and the φ_s are the triplet spin states of orthohydrogen. V' expressed in the form of Eq. (2.8) is given in Table I where, however, that portion of the dipolar term with selection rules $\Delta J = \pm 2$ is neglected, and the part retained gives only $\Delta J = 0$.¹¹ The justification for using the truncated V' follows directly from Eq. (2.15) and the fact that $|\omega_{J,J\pm 2}| \gg |\omega_{\alpha\beta}|$, τ^{-1} for the experimentally used range of pressures (i.e., up to about 200 atm).^{5,7} Thus, an important aspect of the relaxation of orthohydrogen is that the perturbation V' is ineffective in causing transitions where the magnitude of J changes. It is effective only in changing the orientation of J .

The polarization of rotational states by the Zeeman term $\omega_J J_z$ in Eq. (3.1) is negligible (even for magnetic fields of several thousand gauss)¹⁸ compared to $C J^2$ and $K T$, so all states of the same J have about the same energy and are about equally populated at equilibrium. It then follows that $\langle F^{(0)} \rangle = \langle F^{(2)} \rangle = 0$ utilizing Eqs. (2.8), (2.3c), (2.9b).¹⁸ Thus, Eq. (2.15) simplifies considerably because the second term on the right vanishes. Furthermore, it is found that $j_{qq'}(\alpha - \beta) = 0$ for $q \neq q'$. This is consistent with the results of a classical averaging over orientation in isotropic space¹¹ as expected from the principle of spectroscopic stability.¹⁹

There remains an important consideration in the application of Eq. (2.15) to the orthohydrogen problem. The model as formulated means that after a collision there will be a Boltzmann distribution in all the odd J states, independent of initial J states. Experimentally, it is found that changes in magnitude of J are very infrequent.²⁰ If the effect of collisions is considered as just inducing changes of the rotational substates having the same value of J , then for this situation the strong-collision Assumption (4), may be restated: A molecule in a given J state, will, as a result of collision, have equal probability of being in any of its magnetic substates $|m_J\rangle$. Furthermore, since neither the collision process nor the perturbation V is very effective in causing transitions where $\Delta J \neq 0$, it is clear that the relaxation properties of a molecule in a state corresponding to a particular value of J depends only upon

¹⁸ The small effect of polarization that occurs may easily be estimated using the appropriate constants given in N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956), p. 234, and it is found that at about 300°K in a magnetic field of 10 000 G

$$\langle F^{(2)} \rangle_J = 0, \quad |\langle F^{(0)} \rangle_J| \approx J(J+1)/30 \text{ cps},$$

where the averaging is only over rotational states of the same J . Thus the first-order shift of magnetic resonance frequency when Eq. (2.3a) is used is the order of tenths of cycles per second. The other $F^{(q)}$ have no diagonal matrix elements so the corresponding $\langle F^{(q)} \rangle$ always vanish.

¹⁹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), p. 140.

²⁰ R. Brout, J. Chem. Phys. **22**, 934 (1954); I. Zartman, J. Acoust. Soc. Am. **21**, 171 (1949).

¹⁷ In the general quantum-mechanical model of relaxation (see Refs. 11-14) this is proved utilizing the exact conservation of energy whenever energy is transferred from spin to rotational degrees of freedom. In the present case, the uncertainty in energy of the rotational states caused by the collision process prevents the use of such a proof. It would probably be necessary to consider the collision process in more detail.

its redistribution, via these two mechanisms, into the different $|m_J\rangle$. This conclusion is clearly independent of whether the probability of a change in $|m_J\rangle$ per collision is small or large. Then Eq. (2.15) should be rewritten for each set of J states as:

$$j_q^{(J)}(\alpha-\beta) = \frac{1}{2J+1} \sum_{m_J, m_J'} |F_{m_J m_J'}^{(q)}|^2 \frac{\tau_J}{1 + (\omega_{m_J m_J'} + \omega_{\alpha\beta})^2 \tau_J^2}, \quad (3.4)$$

and a separate relaxation equation [(2.14) and (2.16)] may be written for each subensemble of molecules having a different value of J . The subscript on τ_J allows for the possibility of different effective collision times for molecules differing in their J value. The macroscopic magnetization $M(t)$ may now be calculated. In a collection of N molecules,

$$\mathbf{M}_J(t) = B_J N \gamma \hbar \langle \mathbf{I}(t) \rangle_J, \quad (3.5a)$$

and

$$\mathbf{M}(t) = \sum_J \mathbf{M}_J(t), \quad (3.5b)$$

where

$$B_J = \frac{(2J+1) \exp[-\hbar C J(J+1)]}{\sum_{J \text{ odd}} (2J+1) \exp[-\hbar C J(J+1)]} \quad (3.5c)$$

is the fraction of molecules in the J th rotational level and $\langle \mathbf{I}(t) \rangle_J$ is the average value for the J th subensemble. Utilizing Eqs. (2.16),²¹ (2.14), (3.4), and Table I, it is found, following standard procedures,¹¹ that

$$dM_{z,J}^*/dt = -(1/T_{1,J}) \{M_{z,J}^* - B_J M_0\}, \quad (3.6a)$$

and

$$dM_{x,J}^*/dt = -(1/T_{2,J}) M_{x,J}^*, \quad (3.6b)$$

where M_0 is the equilibrium magnetization. $T_{1,J}$ and $T_{2,J}$ are respectively the longitudinal and transverse relaxation times for the J th rotational subensemble, and are

$$\begin{aligned} \frac{1}{T_{1,J}} &= \frac{2}{3} \gamma^2 H'^2 J(J+1) \\ &\times \left[\frac{\tau_J}{1 + (\omega_J - \omega_I)^2 \tau_J^2} + \frac{6}{5} \frac{\gamma^2 H'^2 J(J+1)}{(2J-1)(2J+3)} \right. \\ &\times \left. \left[\frac{\tau_J}{1 + (\omega_J - \omega_I)^2 \tau_J^2} + \frac{4\tau_J}{1 + (\omega_J - \omega_I)^2 4\tau_J^2} \right] \right], \quad (3.7) \end{aligned}$$

²¹ For the orthohydrogen problem it is more convenient to use an operator form of the relaxation equation. This is given by Abragam,¹¹ p. 279, Eqs. 37-41, where, however, his $J_{qq'}(\omega)$ is replaced by $2j_{qq'}(\alpha-\beta)$ of Eq. (2.15) [or its modification Eq. (3.4)]. The assumption that $B(r) = B(r')$ for all the significant terms in Eq. (2.15) must also be made. This is justified for the present case, since matrix elements of V between different J states are negligible.

and

$$\begin{aligned} \frac{1}{T_{2,J}} &= \frac{1}{3} \gamma^2 H'^2 J(J+1) \\ &\times \left[\frac{\tau_J}{1 + (\omega_J - \omega_I)^2 \tau_J^2} + \tau_J \right] + \frac{3}{5} \frac{\gamma^2 H'^2 J(J+1)}{(2J-1)(2J+3)} \\ &\times \left[3\tau_J + 5 \frac{\tau_J}{1 + (\omega_J - \omega_I)^2 \tau_J^2} + \frac{2\tau_J}{1 + (\omega_J - \omega_I)^2 4\tau_J^2} \right]. \quad (3.8) \end{aligned}$$

Equation (3.7) reduces to the SB result¹ for $(\omega_J - \omega_I)^2 \tau_J^2 \ll 1$. It is clear, then, from Eqs. (3.5) to (3.8) that a nonequilibrium magnetization should decay to its equilibrium value with more than one time constant.

It seems reasonable to assume that a strong rf pulse when applied to a gas sample will result in an initial value of $\langle \mathbf{I} \rangle_i$ which is independent of J . In this case Eqs. (3.5) and (3.6) lead to the simple results:

$$[M_z^*(t) - M_0] = (M_{zi} - M_0) \sum_J B_J \exp(-t/T_{1,J}), \quad (3.9a)$$

and

$$M_x^*(t) = M_{xi} \sum_J B_J \exp(-t/T_{2,J}), \quad (3.9b)$$

where

$$\mathbf{M}_i = N \gamma \hbar \langle \mathbf{I} \rangle_i. \quad (3.9c)$$

When Assumption (4) of Sec. 2 may be retained intact, i.e., collisions which change J are important, Eq. (2.13) must include a sum over all odd J states, and it is not correct to treat the relaxation of the different J states separately. In this case, the calculations yields:²¹

$$dM_z^*/dt = -(M_z^* - M_0) \sum_J (B_J/T'_{1,J}), \quad (3.10a)$$

and

$$dM_x^*/dt = -M_x^* \sum_J (B_J/T'_{2,J}), \quad (3.10b)$$

where $T'_{1,J}$ and $T'_{2,J}$ are given by Eqs. (3.7) and (3.8), but the primes indicate that all the τ_J are replaced by τ of Assumptions (4) and (5). Thus, average relaxation times are obtained. Average relaxation times such as these (but essentially with the unprimed $T_{1,J}$ and $T_{2,J}$) have been suggested by BO⁷ as being the appropriate results under the assumption that changes of J are very infrequent, but we have already seen that Eqs. (3.6) to (3.9) are the correct ones under the assumption that they are negligible. This point was not clarified by NO who, indeed, also obtained results like those of Eq. (3.10a).

The physical situation in the case of orthohydrogen may very well lie somewhere intermediate between the extremes given by Eqs. (3.6) and (3.10), so it is of interest to obtain some estimate of how the sum of exponentially decaying functions [Eq. (3.6)] goes over

into an average exponential [Eq. (3.10)]. This problem is reminiscent of the familiar chemical exchange problem in NMR²² except that the difference in Larmor frequencies of molecules in states having different values of J have been taken as negligible,¹⁸ the only difference being in their relaxation properties. As long as collisional transitions rates between J levels are much smaller than $T_{1,J}^{-1}$ and $T_{2,J}^{-1}$, Eqs. (3.6) may easily be modified to include such transitions. We may then regard changes in J as just affecting the populations and therefore the magnetization of the J levels, while the effective relaxation still occurs within a J level. Only the $J=1$ and 3 levels will be considered, so $B_1+B_3=1$, and let τ_1^{-1} and τ_3^{-1} be the rates at which transitions occur from these levels, respectively. Equilibrium considerations lead to $\tau_1/\tau_3=B_1/B_3$, so a mean effective transition rate τ_i^{-1} may be defined by

$$\tau_1=B_3^{-1}\tau_i \quad \text{and} \quad \tau_3=B_1^{-1}\tau_i.$$

[When $\tau_1=\tau_3$, these relations are consistent with Assumptions (4) and (5) of Sec. 2.] Then Eqs. (3.6) become

$$\begin{aligned} d(M_{k,J}^*-B_J M_{k,0})/dt \\ = -[(1/T_{k,J}) + B_J \tau_i^{-1}](M_{k,J}^* - B_J M_{k,0}) \\ + B_J \tau_i^{-1}(M_{k,J'}^* - B_{J'} M_{k,0}), \quad (3.11) \end{aligned}$$

where $J \neq J'=1$ or 3 and $k=x, y$, or z . The general solution of Eq. (3.11), which is rather complex, is given in Appendix II. However, it is found that when $\tau_i^{-1} \ll |T_{k,1}^{-1} - T_{k,3}^{-1}|$, the solution is essentially given by Eq. (3.9), where the $T_{k,J}^{-1}$ are replaced by $\tilde{T}_{k,J}^{-1} = T_{k,J}^{-1} + B_J \tau_i^{-1}$. Although, as already remarked, it is not immediately clear that this treatment applies if $\tau_1, \tau_3 < T_{k,1}, T_{k,3}$, we may hope to get some idea of the limit when τ_i^{-1} is large. Thus, when $\tau_i^{-1} \gg |T_{k,1}^{-1} - T_{k,3}^{-1}|$, the integrated forms of Eqs. (3.10) utilizing the unprimed $T_{k,J}$ in place of the primed ones are the correct solutions of (3.11). It follows also, that the conditions $\tau_1, \tau_3 \gg \tau_J$ do not in themselves imply that transitions changing J have a negligible effect on relaxation, since the conditions $\tau_J \ll T_{k,1}, T_{k,3}$ required for the general validity of Sec. 2 and fulfilled in the experimental work on H_2^{2-4} still permit $\tau_1, \tau_3 \sim T_{k,1}, T_{k,3}$, and these are the conditions under which the equations of BO are appropriate.

The discrepancy of the macroscopic treatment [requiring unprimed $T_{k,J}$ in Eqs. (3.10)] with the strong-collision limit result [$T'_{k,J}$ in Eqs. (3.10)] is readily resolved. When $\tau_1, \tau_3 \sim \tau_J$, then τ_1 and τ_3 are not only important in bringing about an averaging of the relaxation in the different J states, but they will

also contribute a lifetime broadening effect to the rotational states. This latter effect is omitted in the macroscopic treatment, so it is inappropriate unless $\tau_1, \tau_3 \gg \tau_J$. The strong-collision result includes the lifetime effect, but is based on Assumption (4) of Sec. 2, which implies that the rate collisions change the J and m_J values of a molecule, are independent of the initial and final values of m_J , and depend only upon the value of $(2J+1)^{-1}B_J$ for the final J state. The $T'_{k,J}$ in Eq. (3.10) are not really relevant as relaxation times for the different J levels, but they appear as a result of this simplification.

Careful experimental studies would be needed to ascertain the relative importance of collisions which change J . For orthohydrogen at 300°K only the $J=1$ and 3 states need be considered, and $B_{J=3}/B_{J=1}=0.14$, but this ratio rapidly decreases as the temperature is lowered. However, even for room-temperature studies, there has not yet been any definite experimental indication of an effect of the $J=3$ state on the relaxation.^{3,4}

4. APPLICATION TO MORE COMPLEX MOLECULES

Molecules heavier than H_2 are characterized by a closer spacing of the nondegenerate rotational energy levels, and as this spacing decreases, one would expect that collisions will be more effective in causing transitions between them. Furthermore, matrix elements of V between these states would also become increasingly important in the relaxation process. Thus for the heavier molecules, it might be more appropriate to use Assumption (4) of Sec. 2 rather than the modifications discussed in Sec. 3. Clearly the present formulation is limited by allowing only one effective collision time, τ , for each subensemble of molecules which can be approximately treated as isolated from the rotational states accessible to the rest of the ensemble. Such a separation into subensembles might be appropriate for molecules of different nuclear spin symmetry, but it may not always be as clear as in the orthohydrogen case, where to introduce further separations.

In the extension to molecules more complex than H_2 , the rotational wavefunctions ψ_r must be reasonably well known so that the spectral density, Eq. (2.15), may be calculated. In cases where there are internal rotational degrees of freedom ψ_r should include them as well. In this context it is important to recognize a difference that exists between a semiclassical theory of relaxation^{11,12} and the basically quantum-mechanical formulation of the theory presented here. Internal and overall rotations, as treated classically, will tend to average out anisotropic terms such as dipole-dipole interactions, and will lead to spin relaxation effects which are dependent in part on the effective reorientation rates of the motions. However, in the quantum mechanical model, when collisions and related interactions are neglected, the molecule will be in a definite quantum state and no significant spin relaxation is to be expected (barring

²² J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959), Chap. 10, and references cited therein.

the resonance transfer of energy between spin and rotational degrees of freedom via the perturbation V). Significant relaxation is introduced by the effect of collisions which themselves change the molecular rotational states and also broaden them²³ so that V can be effective in nonresonant energy transfers. Thus, in the present formulation the relaxation will depend directly upon the effective collision times causing reorientation and only indirectly on the quantum mechanical rotational frequencies.

The perturbation V in the case of NMR should consist primarily of the dipole-dipole interactions of the nuclear spins, nuclear quadrupole interactions, and the nuclear spin-rotational magnetic coupling.^{8,9} In the case of ESR, electron nuclear dipolar interactions, the electron spin-rotational magnetic coupling and the unquenched spin-orbit coupling should be the dominant terms.²⁴ The magnitude of the electron-spin interactions is much greater (usually of the order of 10^3 greater) than the nuclear spin interactions, and it will not always be true that the condition for the validity of the present theory (i.e., $\tau^{-2} \gg V^2$) is fulfilled.

The application of these considerations to some specific molecules will be discussed elsewhere.

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APPENDIX I

The evaluation of Eq. (2.12) is outlined. Performing the operation Tr_r on the leading term of the double

²³ The broadening in the present theory is clearly a nonsecular, i.e., uncertainty in lifetime, effect. Secular type broadenings resulting from modulation of the rotational energy levels by the intermolecular forces, as well as shifts in these energy levels, would require a theory cast along the lines of Anderson's familiar work: P. W. Anderson, *Phys. Rev.* **76**, 647 (1949).

²⁴ D. Kivelson, *J. Chem. Phys.* **27**, 1087 (1957); **33**, 1094 (1960); M. J. Stephen and G. K. Fraenkel, *ibid.* **32**, 1435 (1960); J. H. Freed and G. K. Fraenkel, *ibid.* **37**, 1156 (1963).

commutator gives:

$$\begin{aligned} & [\text{Tr}_r \{ V^*(t) V^*(t-x) B(r) \sigma^*(t) \}]_{\alpha\alpha'} \\ &= \sum_{\substack{q,q' \\ r,r' \\ \beta,\beta'}} [Z(r) \exp(-E_r/KT) F_{rr',q} F_{r',r,q'}] \\ & \quad \times \exp(-i\omega_{r',r}x) - \langle F^{(q)} \rangle \langle F^{(q')} \rangle] \\ & \quad \times [K_{\alpha\beta}^{(q)} K_{\beta\beta'}^{(q')} \exp(-i\omega_{\beta\beta'}x) \exp(i\omega_{\alpha\beta'}t) \sigma^*(t)_{\beta'\alpha'}], \end{aligned} \quad (\text{A1})$$

where Eqs. (2.9) have been employed. Performing the integrations indicated in Eq. (2.12) yields:

$$\begin{aligned} & \sum_{\substack{q,q' \\ r,r' \\ \beta,\beta'}} \exp[i(\omega_{\alpha\beta} - \omega_{\alpha'\beta'})t] \\ & \quad \times (Z(r) \exp(-E_r/KT) F_{rr',q} F_{r',r,q'}) \\ & \quad \times \{ \tau [1 - i\omega_1\tau] / [1 + (\omega_1\tau)^2] \} \\ & \quad - \langle F^{(q)} \rangle \langle F^{(q')} \rangle \{ \tau [1 - i\omega_{\gamma\beta}\tau] / [1 + (\omega_{\gamma\beta}\tau)^2] \} \} \\ & \quad \times K_{\alpha\gamma}^{(q)} K_{\gamma\beta}^{(q')} \delta_{\alpha'\beta'} \sigma^*(t)_{\beta\beta'}, \end{aligned} \quad (\text{A2})$$

where the dummy indices β and β' have been changed into γ and β , respectively, and $\omega_1 = \omega_{r',r} + \omega_{\gamma\beta}$. The rapidly fluctuating terms for which $\omega_{\alpha\beta} \neq \omega_{\alpha'\beta'}$ are now neglected as are the imaginary terms giving rise to second-order frequency shifts.¹¹⁻¹⁴ When the dummy indices r and r' , q and q' , are interchanged, Eq. (A2) gives the last term on the right in Eq. (2.14). The other terms in Eq. (2.12) are evaluated in a similar manner, but the evenness of ω_1^2 must also be utilized.

APPENDIX II

The general solution to Eq. (3.11) with the condition $\langle \mathbf{I} \rangle_i$ is independent of J is:

$$\begin{aligned} M_k^*(t) - M_{k,0}^* &= [(M_{k,i}^* - M_{k,0})/W_k] \\ & \quad \times \{ [X_k + W_k] \exp[-(Y_k + W_k)t] \\ & \quad - [X_k - W_k] \exp[-(Y_k - W_k)t] \}, \end{aligned}$$

$$W_k^2 = T_{k-}^{-2} + \tau_i^{-2} + 2(1 - 2B_J) T_{k-}^{-1} \tau_i^{-1},$$

$$X_k = (2B_J - 1) T_{k-}^{-1} - \tau_i^{-1},$$

$$Y_k = T_{k+}^{-1} + \tau_i^{-1},$$

where

$$T_{k\pm}^{-1} = T_{k,J}^{-1} \pm T_{k,J'}^{-1}.$$