

Nuclear Magnetic Relaxation in a Gas of Regular Molecules

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(Z. Naturforsch. 25 a, 1169—1177 [1970]; received 15 May 1970)

Nuclear magnetic relaxation (NMR) in a gas of regular (tetrahedral and octahedral) molecules from the point of view of the kinetic theory of transport and relaxation processes based on the Waldmann-Snyder equation is considered. A simple expression is obtained for the spin-rotation interaction based on considerations of the molecular symmetry. The form of the spin-rotation coupling which contains, in addition to the so-called "scalar" coupling constant, also a scalar anisotropy part, Δc , of the spin-rotation coupling tensor determines, along with the collision operator, the form to be taken by an expansion of the nonequilibrium part of the distribution function-density matrix of the gas. Solutions of the set of coupled differential equations which follow upon application of the moment method to the linearized Waldmann-Snyder equation lead to the Bloch equations which define the "spin-lattice" and transverse relaxation times in the gas. Those obtained here are comparable with those obtained using correlation function theory. However, in this work, due to explicit consideration of the molecular symmetry, it is shown that the "effective" spin-rotation coupling coefficient found in tetrahedral and octahedral molecules is not the same and depends in a simple way on the number of equivalent spins in the molecule.

1. Introduction

Traditionally, the theoretical treatment of nuclear magnetic relaxation (NMR) in fluids has utilized the correlation function approach. This procedure has been remarkably successful in describing the various relaxation processes occurring in these media. Of particular interest has been the studies of NMR in polyatomic fluids conducted by BLOOM, HUBBARD, RAMSAY, WAUGH and their co-workers and by TWARD and ARMSTRONG. The correlation function approach has recently been extensively reviewed by BLOOM and OPPENHEIM¹ and by GORDON².

In the past few years there has been a growing interest in an alternative theoretical approach to NMR in fluids, conveniently referred to as the kinetic equation approach (KEA). As is apparent from the foregoing sentence, the KEA involves starting from a proper kinetic equation; for gases, the equation appropriate to NMR calculations is that of

WALDMANN³ and SNIDER⁴. Application of this Waldmann-Snyder equation to spin relaxation processes has been considered by WALDMANN⁵, by CHEN and SNIDER⁶ and by the authors^{7,8}.

The principal advantage arising from the KEA is that the relaxation times are expressed in a natural way in terms of collision integrals similar to those obtained in describing transport processes in polyatomic gases. Other advantages accrue as well: the approximations employed are manifestly physical in nature and are seldom made for mathematical convenience alone; no assumptions need be made regarding the "strength of the molecular collisions". Finally, it might be mentioned that the removal of all approximations made and the extension of the method in order to achieve greater accuracy is fairly straightforward.

The present work deals with NMR in a gas of simple regular molecules in which the dominant relaxation process is that governed by the spin-rotation interaction. The kinetic equation approach is

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¹ M. BLOOM and I. OPPENHEIM, Adv. Chem. Phys. 12, 549 [1967].

² R. G. GORDON, Adv. Mag. Res. 3, 1 [1968].

³ L. WALDMANN, Z. Naturforsch. 12 a, 660 [1957]; 13 a, 609 [1958].

⁴ R. F. SNIDER, J. Chem. Phys. 32, 1051 [1960].

⁵ L. WALDMANN, Nuovo Cim. 14, 898 [1959]; Z. Naturforsch. 15 a, 19 [1960].

⁶ F. M. CHEN and R. F. SNIDER, J. Chem. Phys. 46, 3937 [1967]; 48, 3185 [1968]; 50, 4082 [1969].

⁷ S. HESS, Z. Naturforsch. 23 a, 898 [1968]; Physica 42, 633 [1969].

⁸ S. HESS and F. R. McCOURT, Chem. Phys. Letters 5, 53 [1970].



utilized throughout. By simple regular molecules, it is meant that special emphasis will be given to molecules having tetrahedral (e. g., CH_4 , CF_4) and octahedral (e. g., SF_6 , WF_6) symmetries. Such molecules have a rather complicated intramolecular Hamiltonian describing the internal states. However, many of the terms contained there are quite small and may be neglected in considering gas phase NMR. Those contributions which remain describe rigid rotation of the molecule (governing the Boltzmann distribution of rotational states), centrifugal distortion and the various spin-rotation, spin-spin and (for nuclear spins ≥ 1) quadrupolar couplings. The three latter-mentioned terms provide the dominant relaxation mechanisms. Centrifugal distortion and its rôle in NMR is not considered in this work. In addition to the intramolecular Hamiltonian, there are of course the usual nuclear and rotational terms which make up the Zeeman Hamiltonian.

Section 2 of this paper is devoted to a discussion of the form taken by the spin-rotation coupling in simple regular molecules. The kinetic equation and resulting set of relaxation equations are treated in Section 3 while their solution for the NMR problem is given in Section 4. The fifth Section is devoted to a discussion of the collision integrals and a comparison of the present results with those of BLOOM, BRIDGES and HARDY⁹, DONG and BLOOM¹⁰ and HUBBARD¹¹.

2. The Form of the Spin-Rotation Interaction

The spin-rotation coupling term for a regular molecule has the form

$$\mathcal{H}_{\text{SR}} = \hbar \sum_i \mathbf{s}^{(i)} \cdot \mathbf{C}^{(i)} \cdot \mathbf{J} \quad (2.1)$$

where the summation over i runs over all nuclei situated at equivalent positions in the molecule and where $\mathbf{s}^{(i)}$ and $\mathbf{C}^{(i)}$ represent the individual nuclear spin operator and the spin-rotation coupling tensor at the i^{th} position in the molecule while \mathbf{J} is the rotational angular momentum of the molecule. Now, if \mathbf{e}_i represents a unit vector along the bond-axis joining the i^{th} nucleus to the central nucleus (assumed spinless), the spin-rotation tensor $\mathbf{C}^{(i)}$ can be written in the form

$$\mathbf{C}^{(i)} = c_{\parallel} \mathbf{e}_i \mathbf{e}_i + c_{\perp} (\mathbf{U} - \mathbf{e}_i \mathbf{e}_i) \quad (2.2)$$

where \mathbf{U} is the second rank isotropic ("unit") tensor having as components $U_{ij} = \delta_{ij}$. Expression (2.2) can be rewritten in terms of irreducible Cartesian tensors as

$$\mathbf{C}^{(i)} = c \mathbf{U} + \Delta c \overline{\mathbf{e}_i \mathbf{e}_i}. \quad (2.3)$$

Here c is the average spin-rotation coupling (or the "scalar" coupling) $c = \frac{1}{3}(c_{\parallel} + 2c_{\perp})$ and $\Delta c = c_{\parallel} - c_{\perp}$ represents the anisotropy of the spin-rotation coupling tensor: $\overline{\mathbf{e}_i \mathbf{e}_i} \equiv \mathbf{e}_i \mathbf{e}_i - \frac{1}{3} \mathbf{U}$ is a second rank irreducible tensor (symmetric and traceless).

As the only regular molecules actually occurring are those with tetrahedral and octahedral symmetry, it is useful to consider these two geometries explicitly. For tetrahedral molecules, \mathcal{H}_{SR} has the form

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \sum_{i=1}^4 \mathbf{s}^{(i)} \cdot \mathbf{J} + \Delta c \sum_{i=1}^4 \mathbf{s}^{(i)} \cdot \overline{\mathbf{e}_i \mathbf{e}_i} \cdot \mathbf{J}. \quad (2.4)$$

However, this form is not entirely convenient as it does not show explicitly how the molecular symmetry enters the problem. As only those terms which are unchanged by the operations of the molecular symmetry group, here T_d , can enter into the Hamiltonian, it is best to rewrite Eq. (2.4) in a manner which displays this symmetry. This can be achieved by examining the form taken by the irreducible representations of T_d (see, e. g., Ref. ¹²) and by taking into account the relation $\sum_{i=1}^4 \overline{\mathbf{e}_i \mathbf{e}_i} = 0$ which holds for tetrahedral molecules. The ensuing result is

$$\begin{aligned} \frac{1}{\hbar} \mathcal{H}_{\text{SR}} = & c \mathbf{I} \cdot \mathbf{J} + \Delta c \left\{ \frac{1}{2} \mathbf{I}^{(1)} \cdot (\overline{\mathbf{e}_1 \mathbf{e}_1} + \overline{\mathbf{e}_3 \mathbf{e}_3}) \cdot \mathbf{J} \right. \\ & + \frac{1}{2} \mathbf{I}^{(2)} \cdot (\overline{\mathbf{e}_2 \mathbf{e}_2} + \overline{\mathbf{e}_3 \mathbf{e}_3}) \cdot \mathbf{J} \\ & \left. + \frac{1}{2} \mathbf{I}^{(3)} \cdot (\overline{\mathbf{e}_1 \mathbf{e}_1} + \overline{\mathbf{e}_2 \mathbf{e}_2}) \cdot \mathbf{J} \right\} \end{aligned} \quad (2.5)$$

where \mathbf{I} and the $\mathbf{I}^{(i)}$ ($i = 1, 2, 3$) are defined by

$$\begin{aligned} \mathbf{I} & \equiv \sum_{i=1}^4 \mathbf{s}^{(i)}, & \mathbf{I}^{(1)} & \equiv \mathbf{s}^{(1)} - \mathbf{s}^{(2)} + \mathbf{s}^{(3)} - \mathbf{s}^{(4)}, \\ \mathbf{I}^{(2)} & \equiv -\mathbf{s}^{(1)} + \mathbf{s}^{(2)} + \mathbf{s}^{(3)} - \mathbf{s}^{(4)}, \\ \mathbf{I}^{(3)} & \equiv \mathbf{s}^{(1)} + \mathbf{s}^{(2)} - \mathbf{s}^{(3)} - \mathbf{s}^{(4)}. \end{aligned} \quad (2.6)$$

Equation (2.5) can be written formally as

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \mathbf{I} \cdot \mathbf{J} + \Delta c \mathbf{I}' \cdot \mathbf{J} \quad (2.7)$$

⁹ M. BLOOM, F. BRIDGES, and W. N. HARDY, Can. J. Phys. **45**, 3533 [1967].

¹⁰ R. Y. DONG and M. BLOOM, Can. J. Phys. **48**, 793 [1970].

¹¹ P. S. HUBBARD, Phys. Rev. **131**, 1155 [1963].

¹² C. H. ANDERSON and N. F. RAMSEY, Phys. Rev. **149**, 14 [1966].

with \mathbf{I}' defined by

$$\mathbf{I}' = \frac{1}{2} \{ \mathbf{I}^{(1)} \cdot (\overline{\mathbf{e}_1 \mathbf{e}_1} + \overline{\mathbf{e}_3 \mathbf{e}_3}) + \mathbf{I}^{(2)} \cdot (\overline{\mathbf{e}_2 \mathbf{e}_2} + \overline{\mathbf{e}_3 \mathbf{e}_3}) + \mathbf{I}^{(3)} \cdot (\overline{\mathbf{e}_1 \mathbf{e}_1} + \overline{\mathbf{e}_2 \mathbf{e}_2}) \}. \quad (2.8)$$

Note that this expressions for \mathbf{I}' is symmetric to rotations about the "4" axis*.

Expression (2.7) is identical to that obtained by ANDERSON and RAMSAY¹² as corrected by YI, OZIER and ANDERSON¹³. It is possible to reduce this expression to a still simpler form by utilizing further the molecular symmetry. This is accomplished by using the relation $\sum_{i=1}^4 \overline{\mathbf{e}_i \mathbf{e}_i} = 0$ to replace the pairs of second rank irreducible tensors which accompany $\mathbf{I}^{(1)}$, $\mathbf{I}^{(2)}$ and $\mathbf{I}^{(3)}$ in Eq. (2.8) by the corresponding expressions containing $\overline{\mathbf{e}_4 \mathbf{e}_4}$. Thus \mathbf{I}' becomes

$$\mathbf{I}' = -\frac{1}{2} (\mathbf{I}^{(1)} + \mathbf{I}^{(2)} + \mathbf{I}^{(3)}) \cdot \overline{\mathbf{e}_4 \mathbf{e}_4} - \frac{1}{2} \mathbf{I}^{(1)} \cdot \overline{\mathbf{e}_2 \mathbf{e}_2} - \frac{1}{2} \mathbf{I}^{(2)} \cdot \overline{\mathbf{e}_1 \mathbf{e}_1} - \frac{1}{2} \mathbf{I}^{(3)} \cdot \overline{\mathbf{e}_3 \mathbf{e}_3}. \quad (2.9)$$

If the "4" axis is chosen as the privileged axis so that the K quantum number is defined by the operator J_z (the z -component of \mathbf{J} in the molecular reference frame), then the latter three terms of expression (2.9) represent spin-rotation coupling terms which have off-diagonal matrix elements in the K quantum numbers. Were it not for the presence of the centrifugal stretching term in the Hamiltonian, these matrices would therefore mix the tetrahedral symmetry states for total spin $I = 2, 1$ and 0 and the full expression (2.9) would have to be used in treating the NMR of tetrahedral molecules. However, due to the magnitude of the splitting of the total I symmetry states caused by the centrifugal distortion term, the aforementioned off-diagonal matrices can be safely neglected for the purposes of the present treatment (for a fairly detailed discussion of this see, e. g., Ref. ¹⁰). Hence, the form finally taken by \mathbf{I}' for this problem is

$$\mathbf{I}' = -\frac{1}{2} \tilde{\mathbf{I}} \cdot \overline{\mathbf{e}_4 \mathbf{e}_4} \quad (2.10)$$

where $\tilde{\mathbf{I}}$ is given by

$$\tilde{\mathbf{I}} \equiv \mathbf{I}^{(1)} + \mathbf{I}^{(2)} + \mathbf{I}^{(3)} = \mathbf{s}^{(1)} + \mathbf{s}^{(2)} + \mathbf{s}^{(3)} - 3 \mathbf{s}^{(4)}. \quad (2.11)$$

With this result, the spin-rotation coupling becomes simply

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \mathbf{I} \cdot \mathbf{J} - \frac{1}{2} \Delta c \tilde{\mathbf{I}} \cdot \overline{\mathbf{e}_4 \mathbf{e}_4} \cdot \mathbf{J}. \quad (2.12)$$

In studying gas phase NMR, one further simplification is possible. Classically speaking, this involves taking an average over the rotational motion of the molecule for a given value of J or, quantum mechanically, retaining only that part of the operator

$\overline{\mathbf{e}_4 \mathbf{e}_4}$ which is diagonal with respect to the rotational quantum number, i. e.,

$$(\overline{\mathbf{e}_4 \mathbf{e}_4} \cdot \mathbf{J})_{\text{diag}} = \alpha \mathbf{J}$$

and $\alpha = (J_z^2 - \frac{1}{3} J^2) / J^2$ where J_z (having eigenvalue K) is the component of \mathbf{J} along the molecular figure axis, here taken to be \mathbf{e}_4 . When this has been done, Eq. (2.12) is replaced by

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \mathbf{I} \cdot \mathbf{J} - \frac{1}{2} \Delta c \tilde{\mathbf{I}} \cdot (\alpha \mathbf{J}) \quad (2.13)$$

and it is this form of the spin-rotation coupling which will be employed in the present description of gas phase NMR.

For octahedral molecules, \mathcal{H}_{SR} is given by

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = \sum_{i=1}^6 \mathbf{s}^{(i)} \cdot \mathbf{C}^{(i)} \cdot \mathbf{J}. \quad (2.14)$$

The highly symmetric structure of the molecule allows an immediate replacement of the summation from 1 to 6 by a summation from -3 to $+3$ (excluding zero) and then the spin-rotation interaction takes the form

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \mathbf{I} \cdot \mathbf{J} + \Delta c \sum_{i=1}^3 \mathbf{I}^{(i)} \cdot \overline{\mathbf{e}_i \mathbf{e}_i} \cdot \mathbf{J} \quad (2.15)$$

where the spin operators \mathbf{I} and $\mathbf{I}^{(i)}$ are given in this case by

$$\mathbf{I} \equiv \sum_{i=-3}^{+3} \mathbf{s}^{(i)}, \mathbf{I}^{(i)} \equiv \mathbf{s}^{(i)} + \mathbf{s}^{(-i)}. \quad (2.16)$$

Again, utilizing the molecular symmetry further together with the relation $\sum_{i=1}^3 \overline{\mathbf{e}_i \mathbf{e}_i} = 0$ which holds for octahedral molecules, Eq. (2.15) can be brought

* The explicit forms of the $\mathbf{I}^{(i)}$ in Eqs. (2.6) are required in order to see this symmetry property.

¹³ P.-N. YI, I. OZIER, and C. H. ANDERSON, Phys. Rev. **165**, 92 [1968].

Tetrahedral Molecules	Octahedral Molecules
$[I_\mu^{(i)}, I_\nu^{(j)}]_- = -i \varepsilon_{\mu\nu\lambda} \varepsilon^{ijk} I_\lambda^{(k)} + i \varepsilon_{\mu\nu\lambda} \delta^{ij} I_\lambda$	$[I_\mu^{(i)}, I_\nu^{(j)}]_- = i \varepsilon_{\mu\nu\lambda} \delta^{ij} I_\lambda^{(j)}$
$[I_\mu, I_\nu^{(i)}]_- = i \varepsilon_{\mu\nu\lambda} I_\lambda^{(i)}$	$[I_\mu, I_\nu^{(i)}]_- = i \varepsilon_{\mu\nu\lambda} I_\lambda^{(i)}$
$[I_\mu, \tilde{I}_\nu]_- = i \varepsilon_{\mu\nu\lambda} \tilde{I}_\lambda$	$[I_\mu, \tilde{I}_\nu]_- = i \varepsilon_{\mu\nu\lambda} \tilde{I}_\lambda$
$[\tilde{I}_\mu, \tilde{I}_\nu]_- = 3 i \varepsilon_{\mu\nu\lambda} I_\lambda$	$[\tilde{I}_\mu, \tilde{I}_\nu]_- = i \varepsilon_{\mu\nu\lambda} (2 I_\lambda - \tilde{I}_\lambda)$

Table 1. Commutation relations for the nuclear spin operators.

into a form equivalent to (2.7) where now the "3" axis plays the same rôle as the "4" axis in Eq. (2.7). Thus, the spin-rotation interaction takes the form of Eq. (2.12), viz.,

$$\frac{1}{\hbar} \mathcal{H}_{\text{SR}} = c \mathbf{I} \cdot \mathbf{J} - \frac{1}{2} \Delta c \tilde{\mathbf{I}} \cdot \mathbf{e}_3 \mathbf{e}_3 \cdot \mathbf{J} \quad (2.17)$$

with $\tilde{\mathbf{I}}$ defined in this case by

$$\tilde{\mathbf{I}} \equiv \mathbf{I}^{(1)} + \mathbf{I}^{(2)} + \mathbf{I}^{(3)}. \quad (2.18)$$

An entirely analogous equation to (2.13) can be obtained from Eq. (2.17) where now J_z represents the projection of \mathbf{J} on the "3" axis.

It is worth remarking that if $\tilde{\mathbf{I}}$ is defined in terms of its square and its commutation relations with itself and with \mathbf{I} (see Table 1), the Hamiltonian (2.13) so obtained is independent of the particle labeling and J_z can be defined as the projection of \mathbf{J} on an arbitrary molecule-fixed direction.

3. The Relaxation Equations

A description of NMR is afforded by the equation of motion of the nuclear spin polarization $\langle \mathbf{I} \rangle$. In general, the polarization $\langle A \rangle(\mathbf{r}, t)$ of any operator $A(\mathbf{p}, \mathbf{J}, \mathbf{I}, \tilde{\mathbf{I}})$ is defined as

$$n \langle A \rangle(\mathbf{r}, t) \equiv \text{Tr} \int f A(\mathbf{p}, \mathbf{J}, \mathbf{I}, \tilde{\mathbf{I}}) d\mathbf{p} \quad (3.1)$$

where f is the distribution function-density matrix for the gas and which depends upon position \mathbf{r} , time t , linear momentum \mathbf{p} , and on the rotational and nuclear spin angular momentum operators, \mathbf{J} , \mathbf{I} and $\tilde{\mathbf{I}}$. The symbol Tr designates a trace over all rotational and nuclear spin states.

In polyatomic gases, the distribution function f is governed by the Waldmann-Snider equation which, like its noble gas analogue, the Boltzmann equation, is a nonlinear integro-differential equation. For situations in which f describes only a slight deviation

of the system from equilibrium, this nonlinear equation can be replaced by a linearized version. Most cases of interest and in particular, NMR in gases, fall into this category. That there is only a slight deviation from equilibrium means that f can be written as

$$f = \frac{1}{2} [f^{(0)}, (1 + \Phi)]_+ \quad (3.2)$$

where, in general, the anticommutator of $f^{(0)}$ with $(1 + \Phi)$ is required since the perturbation function Φ need not commute with the equilibrium distribution function $f^{(0)}$. It is important to note that in this case, in contrast to the situation occurring in transport theory, it is necessary to retain in $f^{(0)}$ the complete Hamiltonian for internal states since otherwise the decay of the polarization to its true equilibrium value would not be obtained. The equilibrium distribution function $f^{(0)}$ has the form

$$f^{(0)} = n (2 \pi m k T)^{-3/2} Q^{-1} \exp \left\{ -\frac{p^2}{2 m k T} - \frac{\mathcal{H}}{k T} \right\}. \quad (3.3)$$

Advantage can be taken of the fact that \mathcal{H}_{SR} and $\mathcal{H}_{\text{Zeeman}}$ are very small compared with $k T$ for all gas temperatures and for all field strengths normally employed in experiments on NMR in gases. This fact allows an expansion of the exponential factors containing \mathcal{H}_{SR} and $\mathcal{H}_{\text{Zeeman}}$ to be made; no higher terms than first order ones need be retained. With this, Eq. (3.2) for f can be replaced by

$$f = f_0 \left\{ 1 + \Phi - \frac{\mathcal{H}_{\text{SR}} + \mathcal{H}_{\text{Zeeman}}}{k T} \right\} \quad (3.4)$$

where now f_0 is simply given by

$$f_0 = n (2 \pi m k T)^{-3/2} Q_0^{-1} \exp \left\{ -\frac{p^2}{2 m k T} - \frac{\mathcal{H}_{\text{rot}}}{k T} \right\} \quad (3.5)$$

with Q_0 , the partition function for rotational states, defined as $Q_0 = \text{Tr} \exp \{ -\mathcal{H}_{\text{rot}}/k T \}$.

Linearization of the Waldmann-Snider equation proceeds in the standard way^{14, 6} and need not be described here. The end result, the linearized Waldmann-Snider equation is, for a spatially homogeneous gas,

$$\frac{\partial \Phi}{\partial t} - \frac{1}{i\hbar} [\mathcal{H}_{\text{SR}}, \Phi] - \frac{1}{i\hbar} [\mathcal{H}_{\text{Zeeman}}, \Phi] - \omega(\Phi) = 0. \quad (3.6)$$

The commutators containing \mathcal{H}_{SR} and $\mathcal{H}_{\text{Zeeman}}$ describe the influence of the spin-rotation coupling and the externally applied magnetic field, respectively, on the distribution function, while the quantity ω is a positive definite (super)operator representing the effect of binary collisions in the gas. The specific form of ω is not required for the considerations given at this moment but is, of course, necessary for the calculation of numerical results. Suffice it to say at this point that ω is bilinear in the transition amplitude a (or, equivalently, in the transition operator t) describing a binary collision and that the functional dependence is rather more complicated than the simple differential cross section which appears in the noble gas theory. The precise form of ω will be given in Section 5.

For NMR, the Zeeman Hamiltonian has the form

$$\frac{1}{\hbar} \mathcal{H}_{\text{Zeeman}} = \omega_I \mathbf{h} \cdot \mathbf{I} + \omega_J \mathbf{h} \cdot \mathbf{J} \quad (3.7)$$

where ω_I and ω_J are the precession frequencies $\omega_I = -g_I \mu_N H/\hbar$ and $\omega_J = -g_{\text{rot}} \mu_N H/\hbar$ with g_I , g_{rot} and μ_N being the nuclear and rotational g -factors and the nuclear magneton, respectively, while H is the magnitude of the applied magnetic field

$$\mathbf{H} = H \mathbf{h}.$$

As has already been mentioned, NMR is described by the Bloch equation, i. e., the equation of motion of the nuclear magnetization, which is proportional to the nuclear spin polarization $\langle \mathbf{I} \rangle$. The equation of motion for $\langle \mathbf{I} \rangle$ is obtained in a natural way from the linearized Waldmann-Snider equation by expanding the perturbation function Φ in terms of \mathbf{I} , $\tilde{\mathbf{I}}$ and \mathbf{J} and utilizing the moment method¹⁵. Quantities which are dependent on \mathbf{J} must also be considered since the nuclear spin \mathbf{I} is, for all practi-

cal purposes, unaffected by molecular collisions. The mechanism by which the spin polarization relaxes is a relaxation of the simultaneous polarization of \mathbf{I} and \mathbf{J} by molecular collisions, this being communicated to $\langle \mathbf{I} \rangle$ by means of the spin-rotating coupling. The form which the requisite expansion of Φ must take is, to lowest order, dictated by the moment method and the specific form of the internal state Hamiltonian. In the case under consideration, relaxation through spin-rotation coupling and where c and Δc are small compared with a typical \mathbf{J} -changing collision frequency, the expansion for Φ takes the form

$$\Phi = \mathbf{I} \cdot \mathbf{b} + \mathbf{J} \mathbf{I} : \mathbf{b} + \alpha \mathbf{J} \tilde{\mathbf{I}} : \tilde{\mathbf{b}}. \quad (3.8)$$

In this expansion \mathbf{b} , \mathbf{b} and $\tilde{\mathbf{b}}$ represent the deviations of the polarizations of \mathbf{I} , $\tilde{\mathbf{I}}$ and $\alpha \tilde{\mathbf{I}} \mathbf{J}$ from their equilibrium values. Explicitly \mathbf{b} , \mathbf{b} and $\tilde{\mathbf{b}}$ are given by (see also, e. g., Ref. ⁶)

$$\begin{aligned} \mathbf{b} &= 3(\langle \mathbf{I} \rangle - \langle \mathbf{I} \rangle_{\text{eq}}) / \langle I^2 \rangle_0, \\ \mathbf{b} &= 9(\langle \mathbf{I} \mathbf{J} \rangle - \langle \mathbf{I} \mathbf{J} \rangle_{\text{eq}}) / \langle \tilde{I}^2 J^2 \rangle_0, \\ \tilde{\mathbf{b}} &= 9(\langle \tilde{\mathbf{I}} \alpha \mathbf{J} \rangle - \langle \tilde{\mathbf{I}} \alpha \mathbf{J} \rangle_{\text{eq}}) / \langle \tilde{I}^2 \alpha^2 J^2 \rangle_0. \end{aligned} \quad (3.9)$$

where

$$\langle \tilde{I}^2 \alpha^2 J^2 \rangle_0 = \frac{4}{45} \langle \tilde{I}^2 (J^2 - \frac{3}{4}) \rangle_0.$$

These results are for the "high temperature approximation"^{6, 16}; note, however, that this high temperature approximation is quite valid for gas phase NMR even at liquid nitrogen temperature.

Now, forming moments by bringing in each of the expansion tensors of (3.8) and taking the "scalar product" (i. e., integration over $d\mathbf{p}$ and traces over all quantum states) with the equilibrium distribution function f_0 , a set of relaxation equations is obtained from Eq. (3.6), viz.,

$$\begin{aligned} \frac{\partial \mathbf{b}}{\partial t} - \frac{1}{3} c \langle J^2 \rangle_0 \boldsymbol{\epsilon} : \mathbf{b} + \frac{1}{2} \Delta c \frac{\langle \tilde{I}^2 \alpha^2 J^2 \rangle_0}{3 \langle I^2 \rangle_0} \boldsymbol{\epsilon} : \tilde{\mathbf{b}} \\ - \omega_I \mathbf{h} \times \mathbf{b} = 0, \\ \frac{\partial \mathbf{b}}{\partial t} + c \boldsymbol{\epsilon} : \mathbf{b} + \omega_I \boldsymbol{\epsilon} : \mathbf{h} \mathbf{b} - \omega_J \mathbf{b} \cdot \boldsymbol{\epsilon} \cdot \mathbf{h} + \omega_{\text{coll}} \mathbf{b} = 0, \\ \frac{\partial \tilde{\mathbf{b}}}{\partial t} - \frac{1}{2} \Delta c \boldsymbol{\epsilon} : \mathbf{b} + \omega_I \boldsymbol{\epsilon} : \mathbf{h} \tilde{\mathbf{b}} - \omega_J \tilde{\mathbf{b}} \cdot \boldsymbol{\epsilon} \cdot \mathbf{h} + \tilde{\omega}_{\text{coll}} \tilde{\mathbf{b}} = 0. \end{aligned} \quad (3.10)$$

The results given here are a straightforward generalization of those of CHEN and SNIDER⁶ for the

¹⁴ F. R. MCCOURT and R. F. SNIDER, J. Chem. Phys. **41**, 3185 [1964]; **46**, 2387 [1967]; **47**, 4117 [1967]. — S. HESS and L. WALDMANN, Z. Naturforsch. **21a**, 1529 [1966]; **23a**, 1893 [1968]. — H. H. RAUM and W. E. KÖHLER, Z. Naturforsch. **25a**, 1178 [1970].

¹⁵ L. WALDMANN, Transporterscheinungen in Gasen von mittlerem Druck, in Handb. der Physik, ed. S. FLÜGGE (Springer-Verlag, Berlin 1958); Z. Naturforsch. **18a**, 1033 [1964].

¹⁶ A. ABRAGAM, Principles of Magnetic Resonance, Oxford University Press, London 1961.

diatomic gas, the major differences being the appearance of the Δc term in the first of Eqs. (3.10) and the third equation for $\tilde{\mathbf{b}}$ (which does not appear in the case of a diatomic gas). The quantities ω_{coll} and $\tilde{\omega}_{\text{coll}}$ in these equations are characteristic relaxation frequencies determined by the collision operator and given by

$$\omega_{\text{coll}} \equiv \langle \mathbf{I} \mathbf{J} : \omega(\mathbf{J} \mathbf{I}) \rangle_0 / \langle I^2 J^2 \rangle_0, \quad (3.11)$$

$$\tilde{\omega}_{\text{coll}} \equiv \langle \alpha \tilde{\mathbf{I}} \mathbf{J} : \omega(\alpha \mathbf{J} \tilde{\mathbf{I}}) \rangle_0 / \langle I^2 \alpha^2 J^2 \rangle_0. \quad (3.12)$$

Explicit expressions for these collision integrals will be given in Section 5.

All that is required now is the elimination of the second rank tensors \mathbf{b} and $\tilde{\mathbf{b}}$ from the relaxation equation for \mathbf{b} , thereby obtaining the Bloch equation for the nuclear spin polarization. This is undertaken in the following section.

4. The Bloch Equation

The simplest procedure which can be used in solving Eqs. (3.10) is that in which \mathbf{b} and $\tilde{\mathbf{b}}$ are taken to be constant in a coordinate system which rotates with \mathbf{b} . Such a procedure results in a Lorentzian approximation for the line-shape. The time derivatives of \mathbf{b} and $\tilde{\mathbf{b}}$ are in this approximation given by

$$\frac{\partial \mathbf{b}}{\partial t} = \omega_I (\mathbf{h} \times \mathbf{b} - \mathbf{b} \times \mathbf{h}), \quad \frac{\partial \tilde{\mathbf{b}}}{\partial t} = \omega_I (\mathbf{h} \times \tilde{\mathbf{b}} - \tilde{\mathbf{b}} \times \mathbf{h}), \quad (4.1)$$

so that the latter two of Eqs. (3.10) become

$$\begin{aligned} (\omega_I - \omega_J) \mathbf{b} \cdot \boldsymbol{\epsilon} \cdot \mathbf{h} + c \boldsymbol{\epsilon} \cdot \mathbf{b} + \omega_{\text{coll}} \mathbf{b} &= 0, \\ (\omega_I - \omega_J) \tilde{\mathbf{b}} \cdot \boldsymbol{\epsilon} \cdot \mathbf{h} - \frac{1}{2} \Delta c \boldsymbol{\epsilon} \cdot \mathbf{b} + \tilde{\omega}_{\text{coll}} \tilde{\mathbf{b}} &= 0. \end{aligned} \quad (4.2)$$

These equations can be solved by expanding \mathbf{b} and $\tilde{\mathbf{b}}$ in terms of a closed set of second rank tensors. Thus \mathbf{b} and $\tilde{\mathbf{b}}$ are written as⁶

$$\mathbf{b} = \sum_{i=0}^2 \xi_i \mathbf{b} \cdot \boldsymbol{\epsilon} \cdot \mathfrak{H}^{(i)}, \quad \tilde{\mathbf{b}} = \sum_{i=0}^2 \tilde{\xi}_i \tilde{\mathbf{b}} \cdot \boldsymbol{\epsilon} \cdot \mathfrak{H}^{(i)} \quad (4.3)$$

where

$$\mathfrak{H}^{(0)} = \mathbf{U}, \quad \mathfrak{H}^{(1)} = \mathbf{h} \cdot \boldsymbol{\epsilon}, \quad \mathfrak{H}^{(2)} = \mathfrak{H}^{(1)} \cdot \mathfrak{H}^{(1)} = \mathbf{h} \mathbf{h} - \mathbf{U}. \quad (4.4)$$

Substituting these expansions into Eqs. (4.2), solving the resulting equations for the ξ_i and $\tilde{\xi}_i$ and then introducing the solutions so obtained for \mathbf{b} and $\tilde{\mathbf{b}}$ into the first of Eqs. (3.10) results in the Bloch equation for $\langle \mathbf{I} \rangle$. This Bloch equation can be written formally as

$$\frac{\partial \langle \mathbf{I} \rangle}{\partial t} + g_I \mu_N \mathbf{H} \times \langle \mathbf{I} \rangle + \boldsymbol{\omega}_{\text{SR}} \cdot (\langle \mathbf{I} \rangle - \langle \mathbf{I} \rangle_{\text{eq}}) = 0 \quad (4.5)$$

where the second rank tensor $\boldsymbol{\omega}_{\text{SR}}$ describing the relaxation process is given by

$$\begin{aligned} \boldsymbol{\omega}_{\text{SR}} = \frac{1}{3} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} \left[2 \frac{1}{1+\varphi^2} \mathbf{h} \mathbf{h} + \frac{\varphi}{1+\varphi^2} \mathbf{h} \cdot \boldsymbol{\epsilon} + \left(1 + \frac{1}{1+\varphi^2} \right) (\mathbf{U} - \mathbf{h} \mathbf{h}) \right] \right. \\ \left. + \frac{4}{45} \left(\frac{\Delta c}{c} \right)^2 \frac{q}{4 \tilde{\omega}_{\text{coll}}} \left[2 \frac{1}{1+\tilde{\varphi}^2} \mathbf{h} \mathbf{h} + \frac{\tilde{\varphi}}{1+\tilde{\varphi}^2} \mathbf{h} \cdot \boldsymbol{\epsilon} + \left(1 + \frac{1}{1+\tilde{\varphi}^2} \right) (\mathbf{U} - \mathbf{h} \mathbf{h}) \right] \right\} \end{aligned} \quad (4.6)$$

where $\varphi \equiv \omega/\omega_{\text{coll}}$, $\tilde{\varphi} \equiv \omega/\tilde{\omega}_{\text{coll}}$, $\omega \equiv \omega_I - \omega_J$ and q is the ratio $q \equiv \frac{\langle (J^2 - \frac{3}{2}) \tilde{I}^2 \rangle_0}{\langle J^2 \rangle_0 \langle \tilde{I}^2 \rangle_0}$.

For gases where the molecules are predominantly in rotational states with $J > 2$, q can be approximated by $q \approx \langle \tilde{I}^2 \rangle_0 / \langle I^2 \rangle_0$. From this last equation, the relaxation times T_1 and T_2 and the chemical shift σ are immediately obtained as

$$\frac{1}{T_1} = \frac{3}{2} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} \frac{1}{1+\varphi^2} + \frac{4}{45} \left(\frac{\Delta c}{c} \right)^2 \frac{q}{4 \tilde{\omega}_{\text{coll}}} \frac{1}{1+\tilde{\varphi}^2} \right\}, \quad (4.7)$$

$$\frac{1}{T_2} = \frac{1}{3} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} \left(1 + \frac{1}{1+\varphi^2} \right) + \frac{4}{45} \left(\frac{\Delta c}{c} \right)^2 \frac{q}{4 \tilde{\omega}_{\text{coll}}} \left(1 + \frac{1}{1+\tilde{\varphi}^2} \right) \right\} \quad (4.8)$$

and

$$\sigma = \frac{1}{3} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} \frac{\varphi}{1+\varphi^2} + \frac{4}{45} \left(\frac{\Delta c}{c} \right)^2 \frac{q}{4 \tilde{\omega}_{\text{coll}}} \frac{\tilde{\varphi}}{1+\tilde{\varphi}^2} \right\}. \quad (4.9)$$

In the extreme narrowing limit when $\varphi \ll 1$, $\tilde{\varphi} \ll 1$, T_1 and T_2 are equal and given by

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{T} = \frac{2}{3} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} + \frac{4}{45} \left(\frac{\Delta c}{c} \right)^2 \frac{q}{4 \tilde{\omega}_{\text{coll}}} \right\}. \quad (4.10)$$

These results apply both to tetrahedral and to octahedral molecules: in the former case the ratio q

has the value 3 while in the latter it has the value 2 (for values of $J > 2$). The expressions obtained here

can be compared to the results given by BLOOM, BRIDGES and HARDY⁹ and by BLICHARSKI¹⁷ for tetrahedral molecules. If the expressions given here are evaluated for a single spin, as in CHD₃, then the factors reduce to those obtained by the aforementioned authors. However, no attempt was made there to take into account the equivalent nuclei in the tetrahedral structure and hence their expression differs from those given here by the factor 3/4 arising from $q/4$. Thus, in the extreme narrowing limit $1/T$ is, for tetrahedral molecules,

$$\frac{1}{T} \simeq \frac{2}{3} c^2 \langle J^2 \rangle_0 \left\{ \frac{1}{\omega_{\text{coll}}} + \frac{1}{5} \left(\frac{\Delta c}{c} \right)^2 \frac{1}{\tilde{\omega}_{\text{coll}}} \right\}. \quad (4.11)$$

5. The Collision Integrals

The general form of the collision operator ω has been given by WALDMANN³ and by SNIDER⁴ and as such need not be repeated here. Of particular interest are the collision integrals ω_{coll} and $\tilde{\omega}_{\text{coll}}$ appearing in Eq. (4.6) and defined by Eqs. (3.11) and (3.12). As these are both diagonal collision integrals, they can be written in the form¹⁸

$$\langle \Phi \omega(\Phi) \rangle_0 = n_0^{-1} m_r^{-2} \text{Tr} \{ f_0 f_{01} \Phi \bar{a}(a^\dagger(\Phi + \Phi_1) - (\Phi' + \Phi'_1)a^\dagger) \}, \quad (5.1)$$

where the subscript "1" denotes the colliding partner in a binary collision, m_r is the reduced mass of the colliding pair, \bar{a} essentially the scattering amplitude multiplied by a delta function with respect to the (total) energy¹⁸ and Tr denotes the combined operation of a trace over all quantum states together with integration over the linear momenta of both colliding partners after a collision and their relative momentum before the collision (the trivial integration over the total momentum has already been performed). The primes appearing on Φ' and Φ'_1 in Eq. (5.1) indicate that these quantities are the same function of the linear momenta before a collision that Φ and Φ_1 are after; \bar{a} and a^\dagger are, of course, also functions of the primed variables as well as of the unprimed ones.

As both ω_{coll} and $\tilde{\omega}_{\text{coll}}$ have Φ' s which are independent of the linear momenta, Eq. (5.1) assumes for them the especially simple form

$$\langle \Phi \omega(\Phi) \rangle_0 = n_0^{-1} m_r^{-2} \text{Tr} \{ f_0 f_{01} \Phi \bar{a}[a^\dagger, \Phi + \Phi_1]_- \}. \quad (5.2)$$

Now, if the particular forms of Φ are examined and the fact that the nuclear spin operators \mathbf{I} and $\tilde{\mathbf{I}}$ are essentially unaffected by molecular collisions is taken into account, the expressions for ω_{coll} and $\tilde{\omega}_{\text{coll}}$ of Eqs. (3.11) and (3.12) become

$$\omega_{\text{coll}} = n_0^{-1} m_r^{-2} \text{Tr} \{ f_0 f_{01} \mathbf{J} \cdot \bar{a}[a^\dagger, \mathbf{J}]_- \} / \langle J^2 \rangle_0 \quad (5.3)$$

and

$$\tilde{\omega}_{\text{coll}} = \frac{45 n_0^{-1} m_r^{-2}}{4 \langle J^2 - \frac{3}{4} \rangle} \text{Tr} \{ f_0 f_{01} \alpha \mathbf{J} \cdot \bar{a}[a^\dagger, \alpha \mathbf{J}]_- \}. \quad (5.4)$$

Equations (5.3) and (5.4) show explicitly how ω_{coll} and $\tilde{\omega}_{\text{coll}}$ differ: the collision integral $\tilde{\omega}_{\text{coll}}$ contains, in addition to \mathbf{J} , the quantity $\alpha = (K^2 - \frac{1}{3}J^2)/J^2$. If now, the only collisions occurring are those in which the angle between the molecular figure axis and the direction of \mathbf{J} remains unchanged ($K^2/J^2 = \text{const}$), the summation over the quantum number K can be performed and $\tilde{\omega}_{\text{coll}} = \omega_{\text{coll}}$.

It is worth remarking that if ω_{coll} and $\tilde{\omega}_{\text{coll}}$ are expressed in terms of effective cross sections as

$$\omega_{\text{coll}} = n_0 c_0 \sigma_{\text{eff}}, \quad \tilde{\omega}_{\text{coll}} = n_0 c_0 \tilde{\sigma}_{\text{eff}} \quad (5.5)$$

where c_0 is the thermal velocity $c_0 = [8kT_0/\pi m_r]^{1/2}$, then σ_{eff} represents a cross section for changes in \mathbf{J} during a collision while $\tilde{\sigma}_{\text{eff}}$ represents a cross section which includes an explicit dependence on changes in the angle between \mathbf{J} and the figure axis.

Measurements of the Bloch relaxation times under conditions of magnetic field strength and pressure for which φ and $\tilde{\varphi}$ are not small compared to unity, i. e., when "extreme narrowing" no longer applies, would allow the determination of both ω_{coll} and $\tilde{\omega}_{\text{coll}}$ since there T_1 and T_2 are no longer equal. Such a procedure has been used by HARDY¹⁹ to determine the relaxation times associated with the spin-rotation and dipolar couplings in H₂.

Ideally speaking, the collision integrals (5.3) and (5.4) should now be evaluated for the regular molecules of interest. If this were done and sufficiently accurate values of c obtained from molecular beam measurements, a value of $|\Delta c|$ could be calculated from T_1 or T_2 data in the extreme narrowing limit. At the present moment, unfortunately, there are no collisional calculations available for tetrahedral or octahedral molecules. For a discussion of the collision theory for non-spherical molecules e. g. see

¹⁷ J. S. BLICHARSKI, *Physica* **39**, 161 [1968].

¹⁸ S. HESS, *Z. Naturforsch.* **25 a**, 350 [1970].

¹⁹ W. N. HARDY, *Can. J. Phys.* **44**, 265 [1966].

Ref.²⁰. An alternative procedure, more experimental in nature, would be to calculate theoretically the ratio between ω_{coll} and $\tilde{\omega}_{\text{coll}}$ and then use the low density T_1 and T_2 measurements to obtain experimental values for $|\Delta c|$ and ω_{coll} .

At the present moment, it is still possible to vary parameters in the manner introduced by BLOOM, BRIDGES and HARDY⁹ and employed rather successfully by DONG and BLOOM¹⁰. In this procedure, physical reasoning is employed in order to estimate the ratio of the two collision integrals and then a "best fit" to the minimum in the T_1 versus density curve is obtained by varying $|\Delta c|$ (with c obtained from molecular beam measurements). The same can be done here. If this is done, e. g., for methane then, due to the presence of the additional factors arising from the explicit consideration of the four equivalent proton spins in the molecule, the "best fit" value obtained for $|\Delta c|$ is not 18.2 kHz but rather 21.0 kHz. DONG and BLOOM¹⁰ note that the value 18.2 kHz is the more definitive one as obtained from the molecular beam NMR measurements reported at an APS conference²¹ in 1967 but there does not seem to be a strong reason for believing so since the value 21.0 kHz was obtained not only in the earlier work of ANDERSON and RAMSEY¹² but also by OZIER, CRAPO and LEE²² at a later date. Furthermore, the value of 21.0 kHz seems to have been confirmed by BLOOM and DOROTHY²³. On the other hand, it was carefully pointed out by DONG and BLOOM that the value 18.2 kHz obtained by them could not actually be considered as definitive since they could also obtain a "best fit" for $|\Delta c|$ having the value 21.0 kHz by choosing the ratio of the correlation times to be slightly different from unity, viz., 0.86. They tended, however, to feel that the "equal correlation time" approximation gave the more reliable result.

Another approach to the problem can be attempted by looking more closely at the kinetic theory end. It is possible to attempt to relate the collision integrals occurring in Eq. (4.11) to those measured in the Senftleben-Beenakker effects. A check can be made of the validity of the approximations involved in such an approach if a molecule of the same sym-

metry is available for which both c and $|\Delta c|$ are accurately known. This will be carried out here for CH_4 . In particular, it will be convenient to consider the case when $\omega_{\text{coll}} = \tilde{\omega}_{\text{coll}}$ (in lieu of measurements of both T_1 and T_2 in the non-extreme-narrowing regime). A strongly meaningful calculation is still somewhat frustrated, however, by the unavailability of measurements of the Senftleben-Beenakker effect for the shear viscosity of mixtures of regular molecules with the noble gases since it is the collision bracket obtained there rather than that obtained from the measurements in the pure gas which is analogous to those occurring in NMR. Nonetheless, an attempt can be made by utilizing the ratios as obtained using the rough sphere model—these will still give the qualitative picture.

For the rough sphere model ω_{coll} is given by

$$\omega_{\text{coll}}^{\text{RS}} = 8 n_0 (\kappa + 1) Q_1 \quad (5.6)$$

where κ is the dimensionless moment of inertia parameter $\kappa = 4 I / m \sigma^2$ (m and σ are the mass and diameter associated with the molecule under consideration) and $Q_1 = \sigma^2 (\pi k T / m)^{1/2} (\kappa + 1)^{-2}$. The collision integral occurring in the Senftleben-Beenakker shear viscosity measurements is that for the tensor polarization relaxation¹⁸, ω_T , which is²⁴

$$\omega_T^{\text{RS}} = \frac{4}{3} n_0 (10 \kappa + 3) Q_1. \quad (5.7)$$

Molecule	κ	r_{RS}
CH_4	0.050	1.80
CF_4	0.184	1.47
SiF_4	0.182	1.47
SF_6	0.195	1.45

Table 2.
Some values of κ and r_{RS} .

The ratio of these collision integrals is denoted by r_{RS} and is, therefore,

$$r_{\text{RS}} = \omega_{\text{coll}}^{\text{RS}} / \omega_T^{\text{RS}} = \frac{6(\kappa + 1)}{10 \kappa + 3} \quad (5.8)$$

(values of this ratio for a number of typical regular molecules appear in Table 2). If it is assumed that this ratio remains unchanged in passing from the rough sphere model to a realistic collision model, then the quantity $\langle J^2 \rangle_0 / \omega_{\text{coll}}$ appearing in Eq. (4.11)

²⁰ S. HESS and W. E. KÖHLER, Z. Naturforsch. **23a**, 1903 [1968]. — W. E. KÖHLER, S. HESS, and L. WALDMANN, Z. Naturforsch. **25a**, 336 [1970].

²¹ P.-N. YI, I. OZIER, A. KHOSLA, and N. F. RAMSEY, Bull. Amer. Phys. Soc. **12**, 509 [1967].

²² I. OZIER, L. M. CRAPO, and S. S. LEE, Phys. Rev. **172**, 63 [1968].

²³ M. BLOOM and R. G. DOROTHY, Can. J. Phys. **45**, 3411 [1967].

²⁴ H. MORAAL, F. R. McCOURT, and H. F. P. KNAAP, Physica **45**, 455 [1969].

can be replaced by the corresponding tensor polarization relaxation coefficient $(\omega_T)_{\text{mix}}$ as

$$\frac{\langle J^2 \rangle_0}{\omega_{\text{coll}}} \simeq \frac{2 \langle J^2 (J^2 - \frac{3}{4}) \rangle_0}{3 \tau_{\text{RS}} (\omega_T)_{\text{mix}}}. \quad (5.9)$$

Now, evaluating $\langle J^2 (J^2 - \frac{3}{4}) \rangle_0$ in the classical limit for which

$$\langle J^2 (J^2 - \frac{3}{4}) \rangle_0 \cong \langle J^4 \rangle_0 = \frac{T}{\Theta} I(3) = 2 \frac{T}{\Theta} \quad (5.10)$$

where Θ is the characteristic rotational temperature for the molecule (for CH_4 , $\Theta = 7.8^\circ\text{K}$) and utilizing the rough sphere model once again to get $(\omega_T)_{\text{mix}} = \frac{1}{2}(\omega_T)_{\text{pure gas}}$, T_1 is given (in the extreme narrowing limit) through

$$\frac{1}{T_1} \simeq \frac{16}{9} \left(\frac{T}{\Theta} \right)^2 c^2 \frac{1}{\tau_{\text{RS}} \omega_T} \left\{ 1 + \frac{1}{15} \left(\frac{\Delta c}{c} \right)^2 \right\}. \quad (5.11)$$

For CH_4 , the value of $\omega_T = -n_0 \left[\begin{smallmatrix} 0200 \\ 0200 \end{smallmatrix} \right]$ where $-\left[\begin{smallmatrix} 0200 \\ 0200 \end{smallmatrix} \right]$ is obtained from the work of HULSMAN et al.²⁵ as $1.40 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is, at one atmosphere, given by $\omega_T = 3.75 \times 10^9 \text{ s}^{-1}$ and this, together with the values $c = 10.4 \text{ kHz}$ and $|\Delta c| = 21.0 \text{ kHz}$ given by OZIER, CRAPO and LEE²² leads to a value of T_1 of approximately 14 ms which value should be compared with the value of about 21 ms obtained from Fig. 1 of Ref. ¹⁰. The agreement is quite good considering the crudity of the rough sphere model which has been employed in this calculation. There are a number of possible empirical refinements which could be attempted but none of these seem very promising in view of the fact that accurate measurements are not currently available for many of the regular molecules which could be of interest.

Finally, a comparison of the results found here for T_1 and T_2 with those of other authors should be

made. Prior to the treatment of the spin-rotation coupling in regular molecules given by ANDERSON and RAMSEY¹², it had been assumed that the molecular symmetry in effect played no rôle in determining the final form taken by the relaxation times. The neglect of the rôle of molecular symmetry even led GORDON to an incorrect conclusion that for regular molecules, c_{\parallel} and c_{\perp} are (accidentally) equal and resulted in HUBBARD¹¹ and BLICHARSKI²⁷ (see also ¹⁷) obtaining an incorrect expression for the effective spin-rotation coupling constant. Furthermore, they maintain that their result is valid for all regular molecules! That this is not so is illustrated in this work where the ratio q is 3 for tetrahedral molecules and 2 for octahedral molecules. With the advent of precise measurements of both T_1 and T_2 in the low-density regime, there will be much promise in pursuing these studies further in the hope of being able to extract definitive information about the re-orientation collision integrals in gases of regular molecules and in determining reliable values of $|\Delta c|$ for octahedral molecules such as SF_6 , MoF_6 and WF_6 in the gas phase.

Acknowledgment

Part of the research reported in this paper was done while the authors were at the Kamerlingh Onnes Laboratorium in Leiden, the Netherlands. The authors are indebted to Prof. BEENAKKER for the hospitality extended to them and to the Stichting voor Fundamenteel Onderzoek der Materie (FOM), and to the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (ZWO) for financial support during that period. In addition, one of the authors (F. R. McC.) would like to acknowledge a University of Waterloo Research Grant which has contributed to the completion of this work.

²⁵ H. HULSMAN, E. J. VAN WAASDIJK, A. L. J. BURGMANS, H. F. P. KNAAP, and J. J. M. BEENAKKER, *Physica*, in press.

²⁶ R. G. GORDON, *J. Chem. Phys.* **44**, 1184 [1966].

²⁷ J. S. BLICHARSKI, *Acta Physica Polon.* **24**, 817 [1963].