

Relaxation of nuclear magnetization at low densities^{a)}

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(Received 22 April 1977)

In a recent paper, Tenti and McCourt [J. Chem. Phys. **65**, 623 (1976)] presented theoretical evidence for the existence of a minimum in the transverse relaxation time T_2 of the nuclear magnetization in dilute gases. Here the transverse relaxation rate is reexamined and it is shown that in the low density regime it is impossible to define a T_2 . Moreover, the slowing down of the relaxation rate at low densities is due to a decreasing collision rate and not to a dynamical shift as reported by Tenti and McCourt. It is found that the transverse magnetization behaves as a damped oscillator below a certain critical density. Explicit calculations are presented for H_2 gas and for this system the T_2 description breaks down below 0.02 Torr.

I. INTRODUCTION

Recently, Tenti and McCourt¹ presented a theoretical study of nuclear spin relaxation for very dilute polyatomic gases. The motivation for their work was the realization that as the density (and therefore the collision frequency) is lowered, nuclear spin relaxation must become slower. Tenti and McCourt discuss this in terms of a minimum in the transverse relaxation time T_2 so that eventually, in the limit of zero density, they find that T_2 approaches infinity. Previously, no minimum had been predicted for T_2 and the standard formula^{2,3} incorrectly extrapolate T_2 to zero at zero density.

The failure of previous treatments to satisfy the limiting condition of negligible transverse nuclear spin relaxation rate at low densities raised important theoretical questions. That is, how can the existing theories be amended to include a so-called " T_2 minimum" or, more correctly, what approximations must be re-examined in deriving the transverse relaxation rate in order to correctly describe the low density behavior? The approach by Tenti and McCourt¹ is to start with a generalized master equation valid for dilute gases and for a specific model derive an exact memory kernel. This model and the resulting equations have been studied previously and solved in a weak intramolecular coupling approximation,⁴ which gives the standard results.^{2,3} Tenti and McCourt then calculate a T_1 and T_2 in the usual Markovian approximation by taking the time limit to infinity in the generalized master equation and comparing this with the appropriate frequency limit of the line shape, the half-width of which gives T_1 or T_2 at half-height.

The existence of a T_1 or T_2 depends upon the validity of the Bloch equations. It is shown in this paper that the Bloch equation description fails at densities where the transverse relaxation rate is the largest. The breakdown of the Bloch description occurs because of two related differences between the usual description of relaxation and the low density situation. The first is that at low densities, the correlation time becomes so long it approaches the macroscopic time scale. Thus the Markovian approximation is invalid. The second is that as the density decreases, the collision frequency becomes small in comparison to the intramolecular cou-

pling strength. Hence a weak coupling approximation cannot be used. These two approximations are the ones usually made and, in the work of Tenti and McCourt, they led to incorrect results.

The purpose of this paper is to re-examine the interesting questions raised by Tenti and McCourt and recalculate the transverse magnetization without invoking weak coupling or a Markovian approximation. In general, this is hard to do, but in the model studied the exact solution is easily found. The model, that of a spin $\frac{1}{2}$ system relaxing via the spin rotation intramolecular mechanism, is the same as that used by the Tenti and McCourt and of Ref. 4. Except for making the connection to the former, the notation of the latter reference is followed here.

The exact solution shows that T_2 can only be defined down to a certain pressure below which the system displays complex damped oscillations. These arise from the strong coupling (in comparison to relaxation) between the nuclear spin and rotational states so that the transfer of polarization to the rotational states from the nuclear spin states is returned to the nuclear spin states before relaxation can take place. This results in an oscillation in the magnetization. Such oscillations are usually present in physical systems, but in most cases they are damped out very quickly and neglected as being only initial transients. In fact, the low density behavior of the magnetization results from the persistence of these transient effects to macroscopic times. On the other hand, as expected for linear systems, no regions of instability (i. e., negative relaxation times⁵) exist and, given enough time, the magnetization will decay, but not with a characteristic relaxation time T_1 or T_2 .

For completeness, it must be stated that the Bloch equations are, except for a spin $\frac{1}{2}$ system, only approximations to the true relaxation with the Redfield equations⁶ giving a more exact description. Here it is assumed, as is reasonable for dilute gases, that the Bloch equations give a good description at higher densities and the breakdown at lower densities cannot be explained by going to the (Markovian) Redfield description.

The organization of the paper is as follows: In Sec. II, the model and the exact equations governing it are reviewed. In this section, the connection is made to the work of Tenti and McCourt.¹ Following this, in Sec. III, the exact formal solution, and various limits, are dis-

^{a)}Work supported by the National Research Council of Canada.

cussed analytically. In Sec. IV the exact solutions are studied numerically for the H₂ system. These results clearly illustrate the type of phenomena which occur in the initial transient regime. The discussion, Sec. V, presents the pressure dependence of H₂ in the J=1 rotational state at 61 and 35 Mhz; these results indicate that the low density breakdown of the Bloch equations may be experimentally accessible. Moreover, the theoretical results are not strongly dependent upon the field strength at low density, so that experimentally any convenient Larmor frequency can be used.

II. RELAXATION EQUATIONS

A. Description of the model

The simple example considered here is that of one spin I of magnitude $\frac{1}{2}$ coupled to one rotational state of magnitude J via a spin-rotation intramolecular mechanism,

$$H_c = c I \cdot J = \sum_{m=-1}^1 F^m A^{-m} (-1)^{1-m}, \quad (1)$$

where

$$A^0 = I_z, \quad A^{\pm 1} = (2)^{-1/2} (\mp i) I_{\pm} \quad (2)$$

and

$$F^m = c J^m, \quad J^0 = J_z, \quad J^{\pm 1} = (2)^{-1/2} (\mp i) J_{\pm} \quad (3)$$

Here J_{\pm} and I_{\pm} are the usual raising and lowering operators encountered in angular momentum theory. The restriction to a spin of magnitude $\frac{1}{2}$ has been made since a spin rotation mechanism is known to dominate for this case in the gas phase.⁷

The nonequilibrium internal state density operator for the spin and rotation space must include the various polarizations in the system. For purposes here this is⁸ (the notation is that of Ref. 9)

$$\rho(t) \cong \rho_0 (1 + \mathbf{b}(t) \cdot \mathbf{I} + \mathbf{a}(t) \cdot \mathbf{J} + \mathbf{T}(t) : \mathbf{J}\mathbf{I}) \quad (4)$$

ρ_0 is the equilibrium density operator. This expansion including only vectors in I and J is exact for J=1 and I= $\frac{1}{2}$ and is also a good approximation for general I and J magnitudes. \mathbf{a} , \mathbf{b} , and \mathbf{T} represent, respectively, the nonequilibrium polarizations in J and I and the tensor product IJ describing the correlation between I and J. The observable of interest is the magnetization or, equivalently, its expectation value:

$$\langle \mathbf{I} \rangle(t) = \text{Tr} \rho(t) \mathbf{I} = \frac{1}{3} I(I+1) \mathbf{b}(t) \quad (5)$$

In particular, the time dependence of the transverse magnetization is studied in this work, namely,

$$\langle I_{\pm} \rangle(t) = \frac{i}{3\sqrt{2}} I(I+1) b_{\pm}(t) \quad (6)$$

and this depends upon the polarization of JI and J, namely, $\mathbf{T}(t)$ and $\mathbf{a}(t)$. Defining spherical components of $\mathbf{T}(t)$ [Eq. (79), Ref. 4] as

$$\mathbf{T}(t) : \mathbf{J}\mathbf{I} = \sum_{\alpha\alpha'} \Upsilon_{\alpha\alpha'} J^{-\alpha} A^{-\alpha} (-1)^{\alpha+\alpha'} \quad (7)$$

a set of three coupled equations is obtained by taking moments of the Waldmann¹⁰ Snider¹¹ Boltzmann equation or

of a generalized master equation¹ with the internal Hamiltonian being composed of H_c , and the rotational ($\hbar\omega_J J_z$) and nuclear ($\hbar\omega_I I_z$) Zeeman Hamiltonians. The effect of collisions, via the intermolecular potential, are taken into account by a one relaxation (correlation) time assumption, namely,

$$(\tau')^{-1} = \frac{3}{J(J+1)} \langle \langle \mathbf{J} \cdot \mathbf{R}' | \mathbf{J} \rangle \rangle \quad (8)$$

[cf. Eq. (82), Ref. 4]. For low densities and for one J level this is an excellent approximation which is well borne out by experiment. An important approximation imposed on the collision superoperator R' is that it cannot lead to reorientation of the nuclear spins (i.e., $R'I = 0$). Therefore, relaxation must occur via the intramolecular process. Within this model, the exact set of equations which describe $b_{\pm}(t)$ are [cf. Eqs. (81)–(87) of Ref. 4]

$$\delta b_{\pm}(t)/\delta t = +i\omega_I b_{\pm}(t) + \frac{1}{3} cJ(J+1)(\Upsilon_{01} - \Upsilon_{10}) \quad (9)$$

$$\delta \Upsilon_{10}/\delta t = +i\omega_I \Upsilon_{10} + c b_{\pm}(t) - \Upsilon_{10}/\tau' \quad (10)$$

$$\delta \Upsilon_{01}/\delta t = +i\omega_J \Upsilon_{01} - c b_{\pm}(t) - \Upsilon_{01}/\tau' \quad (11)$$

A similar set of equations can be written down for $\mathbf{a}(t)$, and these also depend upon $\Upsilon(t)$. However, $\mathbf{a}(t)$ does not directly enter into the equations which govern $b_{\pm}(t)$.

The solution to Eqs. (9)–(11) can be found with the initial condition $b_{\pm}(0)$, and $\Upsilon_{10}(0) = \Upsilon_{01}(0) = 0$.

B. Relation to Tenti and McCourt

It is now shown that Eqs. (9)–(11) are exactly equivalent to those used by Tenti and McCourt. This is accomplished by writing Eqs. (18) and (19) of Ref. 1 as

$$\delta b_{\pm}(t)/\delta t = i\omega_I b_{\pm}(t) - \int_0^t dt' K_{\pm}(t-t') b_{\pm}(t') \quad (12)$$

and

$$K_{\pm}(t) = (1/3)c^2 J(J+1) \exp(-t/\tau') [\exp(i\omega_J t) + \exp(i\omega_I t)] \quad (13)$$

which define K^{01} and K^{10} , respectively:

$$K_{\pm}(t) \equiv \frac{1}{3} cJ(J+1) [K_1^{01}(t) + K_1^{10}(t)] \quad (13)$$

where the identifications $\Delta M_{\pm}(t) \rightarrow b_{\pm}(t)$, $\nu_c \rightarrow 1/\tau'$, and $\omega_{SR} \rightarrow c$ are made. It is easily verified that

$$\Upsilon_{10}(t) = \int_0^t dt' K_1^{10}(t-t') b_{\pm}(t') \quad (14)$$

and

$$\Upsilon_{01}(t) = - \int_0^t dt' K_1^{01}(t-t') b_{\pm}(t') \quad (15)$$

so that

$$\frac{1}{3} cJ(J+1) (\Upsilon_{10} - \Upsilon_{01}) = \int_0^t dt' K_{\pm}(t-t') b_{\pm}(t') \quad (16)$$

It follows that Eq. (12) is identical to Eq. (9) with the memory integral of the generalized master equation¹² determined from Eqs. (10) and (11). Thus the set of Eqs. (9)–(11) is exactly equivalent to those of Tenti and McCourt¹ and of Ref. 4. It is in the solutions of either Eqs. (9)–(11) or Eq. (12) where important differences arise between Ref. 1 and the work here.

III. FORMAL SOLUTIONS FOR THE TRANSVERSE MAGNETIZATION

A. Exact solution

Equations (9)–(11) can be written in matrix form,

$$\delta \mathbf{A} / \delta t = -\mathbf{R} \cdot \mathbf{A}, \tag{17}$$

where

$$\mathbf{A} = \begin{pmatrix} b_1 \\ \Upsilon_{10} \\ \Upsilon_{01} \end{pmatrix}; \quad \mathbf{R} = \begin{pmatrix} -i\omega_I + \frac{1}{3}cJ(J+1) & -\frac{1}{3}cJ(J+1) \\ -c & -i\omega_I + 1/\tau' & 0 \\ +c & 0 & -i\omega_J + 1/\tau' \end{pmatrix} \tag{18}$$

and, subject to the initial condition,

$$\mathbf{A}(0) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} b_1(0) \tag{19}$$

solved exactly by standard methods.⁵ That is, a matrix \mathbf{T} is found which diagonalizes \mathbf{R} ,

$$(\mathbf{T} \cdot \mathbf{R} \cdot \mathbf{T}^{-1})_{ij} = \lambda_i \delta_{ij}, \tag{20}$$

so that, with Eq. (19) written as

$$\mathbf{T} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} b_1(0) = \begin{pmatrix} T_{11}(0) \\ T_{21}(0) \\ T_{31}(0) \end{pmatrix} b_1(0), \tag{21}$$

the solution is

$$\begin{pmatrix} b_1(t) \\ \Upsilon_{10}(t) \\ \Upsilon_{01}(t) \end{pmatrix} = \mathbf{T}^{-1} \begin{pmatrix} T_{11}(0) e^{-\lambda_1 t} \\ T_{21}(0) e^{-\lambda_2 t} \\ T_{31}(0) e^{-\lambda_3 t} \end{pmatrix} b_1(0). \tag{22}$$

Specifically, the time dependence of the transverse magnetization is

$$b_1(t) = \sum_{i=1}^3 J_{11}^{(i)} \exp(-\lambda_i t) b_1(0). \tag{23}$$

The quantities $J_{\mu\lambda}^{(i)}$ are obtained from the diagonalization procedure, viz.,

$$J_{\mu\lambda}^{(i)} = T_{\mu i} (T^{-1})_{i\lambda} \tag{24}$$

being the residues of the spectral density $J_{\mu\nu}$.

B. Perturbative solution

Previously,⁴ the 3×3 matrix has been solved to second order in the spin rotation coupling strength c . For small c , the approximate eigenvalues are^{4,5}

$$\begin{aligned} \lambda_1 &\cong -i\omega_I + (1/3)c^2 J(J+1) \tau' \{1 + [1 + i(\omega_I - \omega_J) \tau']^{-1}\}, \\ \lambda_2 &\cong -i\omega_I + \tau'^{-1} - (1/3)c^2 J(J+1) \tau', \\ \lambda_3 &\cong -i\omega_J + \tau'^{-1} - (1/3)c^2 J(J+1) \tau' [1 + i(\omega_I - \omega_J) \tau']^{-1}. \end{aligned} \tag{25}$$

Since, in this regime, $\tau'^{-1} \gg c^2 \tau'$, it is clear that $\text{Re}(\lambda_2)$, $\text{Re}(\lambda_3) \gg \text{Re}(\lambda_1)$, so that contributions from λ_2 and λ_3 rapidly decay. Hence the approximate solution to Eq. (23) after the transients have decayed away is⁴

$$b_1(t) \cong e^{-t/T_2} e^{i\omega_I(1-\sigma)t} b_1(0), \tag{26}$$

where the transverse relaxation rate is defined as

$$\frac{1}{T_2} = (1/3)c^2 J(J+1) \left(\tau' + \frac{\tau'}{1 + (\omega_I - \omega_J)^2 \tau'^2} \right), \tag{27}$$

and a dynamical shift is given by

$$\sigma = - (1/3)c^2 J(J+1) \omega_I^{-1} (\omega_I - \omega_J) \tau'^2 [1 + (\omega_I - \omega_J)^2 \tau'^2]^{-1}. \tag{28}$$

Equation (27) for T_2^{-1} is the expression usually obtained for the transverse relaxation rate for a spin rotation mechanism.

In the opposite limit for $\tau'^{-1} \ll c$, the approximate eigenvalues are

$$\begin{aligned} \lambda_1 &\cong (2\tau')^{-1} - i(\omega_I + \delta), \\ \lambda_2 &\cong (2\tau')^{-1} - i(\omega_I - \delta), \\ \lambda_3 &\cong \tau'^{-1} - i\omega_J, \end{aligned} \tag{29}$$

while the dynamical shift is now

$$\delta \cong [1/3 J(J+1)]^{1/2} c. \tag{30}$$

These approximate eigenvalues are derived assuming that $|\omega_I - \omega_J| \gg 1/3J(J+1)c^2$ which is satisfied for most experimental situations.

For zero magnetic field strength (i.e., $\omega_I = \omega_J = 0$), the exact eigenvalues are easily computed to be $1/\tau'$, $1/(2\tau') \pm 1/2[1/\tau'^2 - 8/3J(J+1)c^2]^{1/2}$. Clearly, all three eigenvalues are positive, while two become complex when $1/\tau'^2 < 8/3J(J+1)c^2$. At this point, the transverse magnetization changes from aperiodic relaxation to damped oscillation.

The general (nonzero magnetic field) time dependence of solution Eq. (23) depends upon the roots of the characteristic equation. It is easily shown that the real parts of λ_i are positive (and the solution is stable) by the application of the Hurwitz criterion⁵ to the real part of the matrix, Eq. (18). However, the general eigenvalues are complex, with the most rapid time dependence arising from ω_I (since $\omega_I > \omega_J$ in all physical situations). If the time dependence due to ω_I is removed by passing to the rotating frame, and studying $\hat{b}_1(t) \equiv e^{i\omega_I t} b_1(t)$, it is found that the solution displays aperiodic motion (in fact, exponential decay) until the imaginary parts of the eigenvalues become large in comparison to the real parts. The imaginary parts can be interpreted as dynamical frequency shifts. As shown in Eq. (30), when $\tau'^{-1} \ll c$, the shifts are independent of τ' and these lead to a periodic time dependence of $\hat{b}_1(t)$ for small τ'^{-1} [cf. Eq. (29)]. When this happens, the Bloch equation description breaks down and $\hat{b}_1(t)$ displays damped oscillatory motion. Moreover, it is clear that in the limit of small τ'^{-1} , the real parts of the three eigenvalues, Eq. (29), are comparable in size and the full equation (23) must be used rather than the approximation, Eq. (26). Certainly it is impossible to define a T_2^{-1} as $\tau'^{-1} \rightarrow 0$ or even to extrapolate from T_2^{-1} , Eq. (27), to small τ'^{-1} . In particular, the relaxation at small τ'^{-1} is governed by τ'^{-1} directly and not by $c^2 \tau'^{-1}$ as in Eq. (27).

IV. NUMERICAL CALCULATIONS

In this section the exact numerical solutions to Eqs. (9)–(11) are presented. To do this, it is necessary to specify the parameters τ' and c which are chosen here to

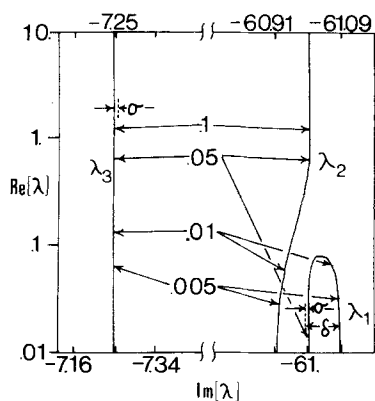


FIG. 1. The loci of the three complex eigenvalues as a function of gas pressure given in torr.

be appropriate for H_2 gas. In particular, the spin rotation coupling constant is taken as $c = 0.115$ Mhz and the correlation time as $\tau' = 8.0 \times 10^{-6}/p$ sec, where the gas pressure p is given in torr. These values of c and τ' are chosen for illustrative purposes only and contributions from other mechanisms are not included. Moreover, we restrict the study to $J=1$ and choose ω_I to be 61 MHz (hence ω_J is 7.25 MHz).

Having fixed the parameters τ' , c , and ω_I and ω_J , the only variable remaining is the density ρ or pressure $p = \rho kT$. The exact numerical solutions are obtained by following the procedure outlined in Sec. III A and varying the density. At a given pressure, the time dependence of $b_1(t)$ is governed by the eigenvalues λ_i , Eq. (23). These are plotted in the complex plane in Fig. 1, with the regions in the neighborhood of $\omega_J = 7.25$ Mhz and $\omega_I = 61$ Mhz expanded to exaggerate the dynamical shifts. These exact eigenvalues show that λ_2 and λ_3 move further off the imaginary axis with increasing pressure. Hence they act as initial transients at pressures greater than about 0.02 torr. On the other hand, $\text{Re}(\lambda_1)$ first in-

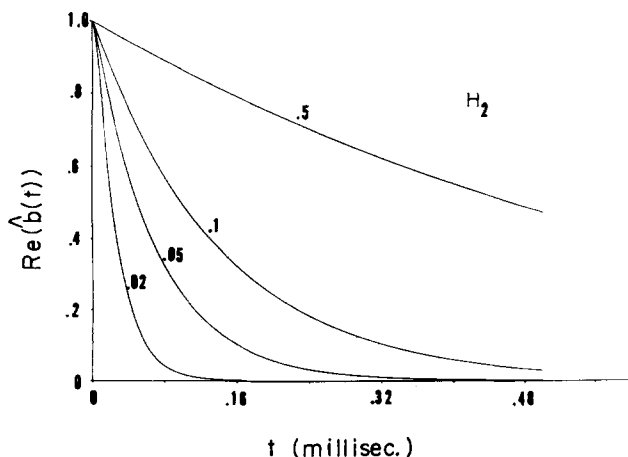


FIG. 2. The time dependence of the real part of transverse magnetization in the rotating frame of ω_I from 0.5 to 0.02 torr.

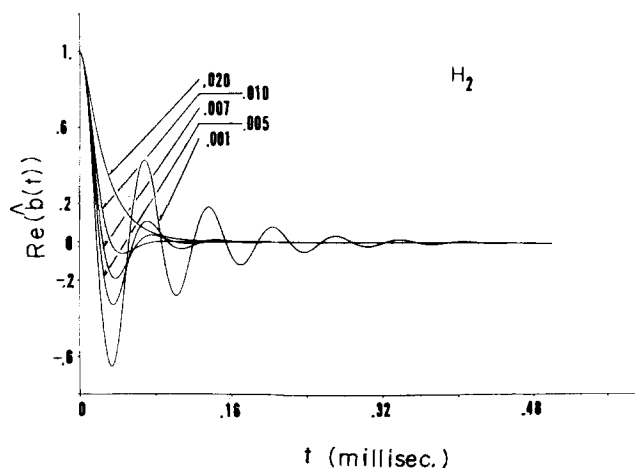


FIG. 3. The same as Fig. 2 but for pressures from 0.02 to 0.002 torr.

creases with increasing pressure and then, after passing through a maximum at about 0.015 torr, returns to the imaginary axis. Clearly, λ_1 dominates the long time dependence at pressures greater than 0.02 torr. However, the real parts of all three eigenvalues are comparable in size at 0.01 torr and lower pressures. Their respective contributions to $b_1(t)$ depend upon the relative weightings $J_{11}^{(i)}$. These are obtained from the eigenfunctions, cf. Eq. (24). They are discussed in detail elsewhere.¹³ One important aspect is that $J_{11}^{(3)}$ (the λ_3 residue) has a very small weight relative to the λ_1 and λ_2 terms. This is a consequence of the fact that λ_1 and λ_2 oscillate at about ω_I , which is out of phase with the ω_J frequency of λ_3 and results in the coupling between $b_1(t)$ and $\Upsilon_{10}(t)$ being much greater than between $b_1(t)$ and $\Upsilon_{01}(t)$ [cf. Eq. (18)].

In order to study the time dependence of $b_1(t)$, the rapidly oscillating contribution from ω_I is removed by passing to the rotating frame,

$$\hat{b}_1(t) = e^{i\omega_I t} b_1(t) . \quad (31)$$

$\text{Re}[\hat{b}_1(t)]$ is plotted in Figs. 2 and 3 as a function of time up to 0.5 msec. The curves for pressures $p = 0.02$ torr and greater display exponential decay, as can be seen from Fig. 4, where $-\text{Re}\{\ln[\hat{b}_1(t)]\}$ is plotted as a function for t for the same densities as in Fig. 2. The slope of the lines in Fig. 4 gives T_2^{-1} [Eq. (27)]. On the other hand, for densities lower than 0.02 torr in Figs. 4 and 5 it is clear that exponential behavior no longer occurs. The most efficient relaxation is at about 0.01 torr, where the transverse magnetization has effectively died out after 8×10^{-5} sec.

At lower densities than 0.01 torr, the relaxation slows down and the transverse magnetization becomes a damped oscillator. This can be understood from the density dependences of the eigenvalues in Fig. 1. At high densities when λ_1 dominates, the dynamical frequency shift is very small [cf. Eq. (28)] in comparison to $\text{Re}(\lambda_1) \approx 1/T_2$. At the opposite limit, when τ'^{-1} becomes small, the dynamical shift becomes the pressure independent quantity in Eq. (30). This shift leads to the

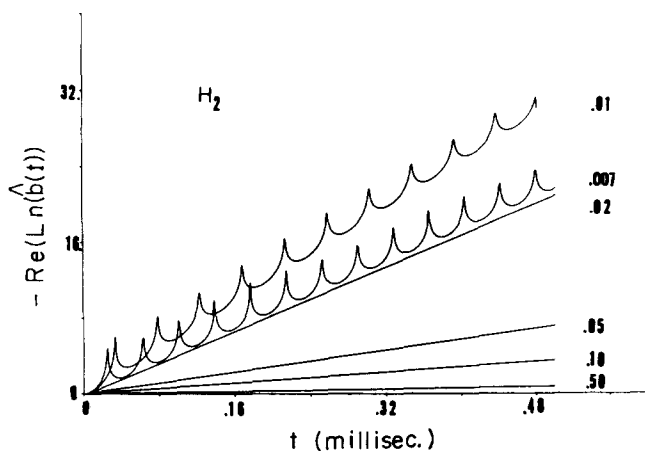


FIG. 4. The time dependence of the negative of the real part of the natural logarithm of the transverse magnetization from 0.5 to 0.007 torr.

oscillatory motion shown in Fig. 2 when $\text{Re}(\lambda_i) \approx \text{Im}(\lambda_i)$ and

$$\hat{b}_1(t) \cong e^{-t/(2\tau')} \left(\cos(\delta t) + \frac{1}{2\delta\tau'} \sin(\delta t) \right) b_1(0). \quad (32)$$

For the numerical choice of parameters here, it is seen from Fig. 1 that the dynamical shift becomes comparable to $\text{Re}(\lambda_i)$ at densities less than 0.02 torr, below which the oscillatory motion sets in as seen in Fig. 3.

V. DISCUSSION

In this work, the very low density behavior of the transverse magnetization for an exactly solvable model of H_2 gas with a spin rotation intramolecular mechanism and a single relaxation time has been studied. It is found that at densities such that the product of the correlation time and the intramolecular coupling strength is large ($\tau'c \gg 1$), a weak coupling perturbative solution cannot be invoked and the exact solution must be found. This shows that as a result of the persistence of transient effects to macroscopic times at low densities, a single T_2^{-1} cannot be defined below 0.02 torr. However, below 0.02 torr, the relaxation rate reaches a maximum

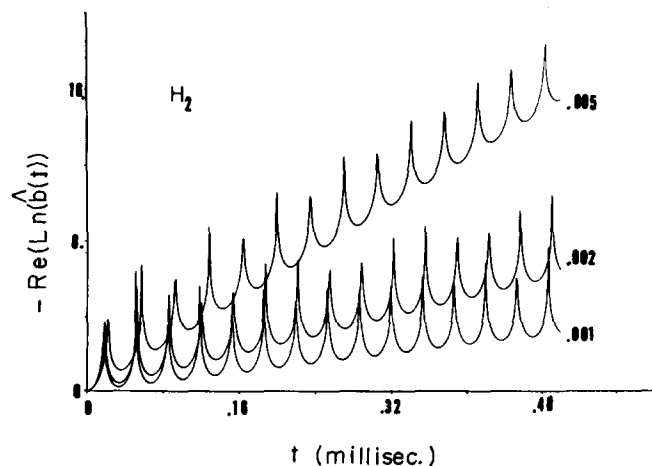


FIG. 5. The same as Fig. 4 but for pressures of 0.002 and 0.005 torr.

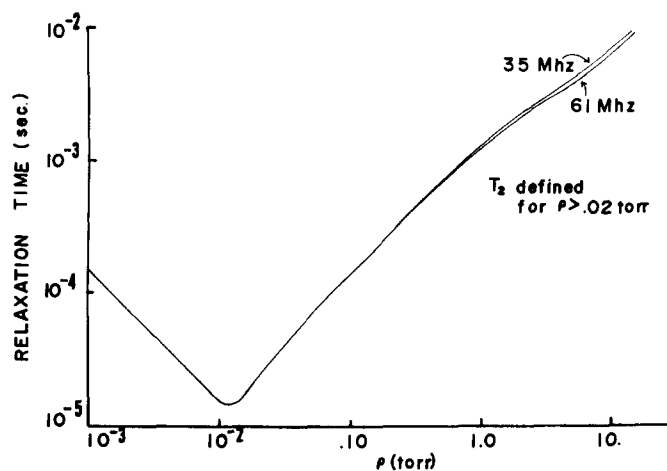


FIG. 6. The inverse of the relaxation rate for the transverse magnetization as a function of pressure for $\omega_j = 61$ and 36 MHz.

at about 0.01 torr, after which, for lower pressures, the relaxation slows down and acts like a damped oscillator.

It is also shown in this calculation that components oscillating at similar frequencies, namely, $b_1(t)$ and $T_{10}(t)$, are strongly coupled, whereas those oscillating at very different frequencies, $b_1(t)$ and $T_{01}(t)$, are weakly coupled.

The dynamical shift is found to be very small at all densities. However, the shift becomes independent of density at low densities and is responsible for the oscillatory motion described in Sec. IV. It is *not* responsible for the slow decay rate of the nuclear spin at low densities.

The time dependences of Υ and $\mathbf{a}(t)$ have not been treated here. This is because Υ is not related to a standardly measured observable (i. e., $\propto \langle \mathbf{I} \cdot \mathbf{J} \rangle$), while $\mathbf{a}(t) \propto \langle \mathbf{J} \rangle$, in contrast to $b_1(t)$, can relax directly through collisions without having to rely on an intramolecular process.

The study here has concentrated solely on the pressure dependence with fixed, physically reasonable, values for $\tau'p = \text{const}$ and c . A similar study could be undertaken by varying c or $\tau'p$. Such extensions are not treated since studying a large enough range of the density p is equivalent to varying c or $\tau'p$.

This work was motivated by the observation by Tenti and McCourt¹ that at low densities the transverse magnetization must vanish. Their approach is based upon a calculation of a T_2 . Here it has been shown that the nuclear spin does not decay exponentially at low densities, so specifying a single relaxation time has very little meaning.

Finally, in Fig. 6, a plot of the density dependence of the relaxation rate is given. The plot is obtained by taking the slope of the curves in Figs. 4 and 5. The relaxation rates at pressures below 0.02 torr are obtained by taking the slope at the bottom of the oscillations in Fig. 4. It must be stressed that at low densities, wall relaxation can play an important role. Neither these ef-

fects nor mechanisms other than a spin rotation process have been taken into account. However, the calculation here indicates the relaxation is exponential down to at least 0.02 torr at which density $T_2 \cong 5 \times 10^{-4}$ sec for H_2 gas in the $J=1$ state. At this pressure, this theoretical result is independent of the choice of the magnetic field strength, so any experimentally convenient value of the field can be used¹⁴ as long as $(\omega_I - \omega_J) \tau' \gg 1$.

ACKNOWLEDGMENTS

The author wishes to thank Professor R. F. Snider and Professor B. C. Eu for helpful discussions. The financial support of the National Research Council of Canada is greatly appreciated.

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¹⁴The values of $\omega_I = 35$ and 61 MHz were suggested by R. Armstrong as being experimentally typical.