

ACCURATE LOW DENSITY CALCULATIONS OF THE TRANSVERSE NUCLEAR MAGNETIC RELAXATION OF H_2 †

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Accurate low density theoretical calculations are presented for the transverse nuclear magnetic relaxation of H_2 . It is shown that resonances about ν_J , $|2\nu_J - \nu_J|$ and $2\nu_J - \nu_J$ exist in addition to the usual ν_J mode. These resonances lead to suggestions for experimental detection of the non-exponentiality of the transverse relaxation at low densities.

1. Introduction

The low density nuclear magnetic relaxation of gases displays non-exponential behaviour. The effects arise from the persistence of the "lattice" degrees of freedom to macroscopic times [1]. These usually decay out as initial transients at higher densities. Theoretical interest [1–5] in these effects is partly a result of the re-evaluation and modification of the usual expression [6] for T_2 which incorrectly extrapolates to zero at zero density [2]. Recent experiments by Armstrong and Kalechstein [7] have attempted to detect the non-exponentiality of the transverse relaxation time for H_2 . They report that down to 0.05 amagat, no detectable deviation from the standard expression [7–9] for T_2^{-1} occurs. On the other hand, it is possible to calculate theoretically, at different pressures, the exact transverse NMR spectrum for H_2 . It is the purpose of this article to present these calculations in both the time and frequency domain.

Moreover, new suggestions are made as to how these effects may be detected. Previously [4,7] attention was focussed on the resonance frequency of the nuclear spins, ν_J . This mode dies with decreasing pressure and the deviations from lorentzian shape are difficult to detect [7]. However, it is shown here that as the resonance peak dies, with decreasing pressure, other peaks, located at ν_J , $|2\nu_J - \nu_J|$, and $2\nu_J - \nu_J$, start to grow. Any detec-

tion of these resonances would be confirmation of the breakdown of the Bloch description and experimental confirmation of the theory.

Recently the problem has been studied numerically for H_2 by McCourt and Tenti [4] using a single relaxation time approximation (SRTA). Their treatment is restricted to the study of the dominant mode about ν_J . In the present paper the full spectrum is calculated, including the interaction between the rotational levels $J=1$ and 3, the different relaxation rates from the Bloom–Oppenheim theory [8,9], and both the spin–rotation and dipole–dipole mechanisms. The two relaxation mechanisms lead to complicated spectra at low densities.

In the following section, the equations describing the transverse relaxation are set up for an n -level system [9,10] and the method of solution explained. Only scant attention is paid to the theoretical developments since they have been adequately explained elsewhere [1,3,5]. However, the connection to the Bloom–Oppenheim [9] theory is made in the appendix. The numerical calculations and results are given in section 3, and suggestions for experimental detection of the results are made in section 4. A discussion concludes the paper.

2. Generalized two level theory for hydrogen

The Bloom–Oppenheim theory [9] for molecular hydrogen derives expressions for the spectral densities.

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These determine the nuclear spin relaxation rates in terms of collisional rate constants between the $J=1$ and 3 rotational levels. When solved in the limit of weak intramolecular coupling, T_1^{-1} and T_2^{-1} are obtained. Equivalently, one can start from the kinetic theory approach [10] and the same expressions are obtained when the appropriate identification is made between the collisional relaxation times and the Bloom–Oppenheim rate constants [10].

In this work, as in ref. [1], a set of differential equations is presented. These equations describe the two dominant intramolecular mechanisms that lead to the transverse relaxation. Application [7] of the Bloom–Oppenheim theory [9] provides the parameters needed to solve the differential equations exactly. These values are known to give an excellent description of H₂ in the Bloch regime (i.e., that density range where T_1 and T_2 are well defined). The difference in the approach here is that the weak coupling approximation is not made as in the other theories [9,10].

As the starting point, a set of differential equations is used to describe the magnetization, $\mathbf{b}(t) = [\frac{1}{3}I(I+1)]^{-1} (\langle \mathbf{I} \rangle(t) - \langle \mathbf{I} \rangle_{\text{eq}})$, and the other degrees of freedom of the system which are coupled to the nuclear spin. Here $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$ for the two proton spins. The appropriate equations have been derived by Chen and Snider [10]. The transverse component of the magnetization [3], $b_1(t) = -i(2)^{3/2} \langle J_+ \rangle$ can be written for the spin–rotation mechanism as

$$\frac{\partial b_1}{\partial t} = i\omega_I b_1 + \frac{1}{3}c \sum_{J=1}^{\infty} J(J+1) P_J (\Upsilon_{01}^J - \Upsilon_{10}^J). \quad (1)$$

$$\frac{\partial \Upsilon_{10}^J}{\partial t} = i\omega_I \Upsilon_{10}^J + c b_1 - \sum_{J'=1}^{\infty} \Upsilon_{10}^{J'} / \tau_{JJ'}^{\prime\prime}. \quad (2)$$

$$\frac{\partial \Upsilon_{01}^J}{\partial t} = i\omega_I \Upsilon_{01}^J - c b_1 - \sum_{J'=1}^{\infty} \Upsilon_{01}^{J'} / \tau_{JJ'}^{\prime\prime}. \quad (3)$$

Here c is the spin–rotation coupling constant, where $c = -\gamma_I H'$, $\omega = 2\pi\nu$, P_J is the Boltzmann factor, and Υ_{pq}^J are defined as the spherical components of the simultaneous polarization of I and J [10]. The first index refers to the spin I and the second to the rotational angular momentum J . These equations are the spherical components of eqs. (60) and (61) of ref. [10].

Similarly for the dipole–dipole mechanism, the set

of equations is

$$\frac{\partial b_1}{\partial t} = i\omega_I b_1 - \frac{c_d}{20\sqrt{3}} \sum_J P_J J(J+1) \times [(G_{01}^J - G_{10}^J) - \sqrt{\frac{2}{3}}(G_{-12}^J - G_{2-1}^J)], \quad (4)$$

$$\frac{\partial G_{10}^J}{\partial t} = c_d d_J \frac{1}{2} \sqrt{3} b_1 + i\omega_I G_{10}^J - \sum_{J' \text{ odd}} G_{10}^{J'} / \tau_{JJ'}^{\prime\prime}, \quad (5)$$

$$\frac{\partial G_{01}^J}{\partial t} = -c_d d_J \frac{1}{2} \sqrt{3} b_1 + i\omega_I G_{01}^J - \sum_{J' \text{ odd}} G_{01}^{J'} / \tau_{JJ'}^{\prime\prime}, \quad (6)$$

$$\frac{\partial G_{-12}^J}{\partial t} = \frac{c_d d_J b_1}{\sqrt{2}} + i(2\omega_I - \omega_J) G_{-12}^J - \sum_{J' \text{ odd}} G_{-12}^{J'} / \tau_{JJ'}^{\prime\prime}, \quad (7)$$

$$\frac{\partial G_{2-1}^J}{\partial t} = -\frac{c_d d_J b_1}{\sqrt{2}} + i(2\omega_J - \omega_I) G_{2-1}^J - \sum_{J' \text{ odd}} G_{2-1}^{J'} / \tau_{JJ'}^{\prime\prime}. \quad (8)$$

Again these are obtained as the spherical equivalents of the equations in ref. [10] with G_{pq}^J describing the “lattice” polarization. In the above equations, ω_I and ω_J are the Larmour frequencies, $c_d = -6\gamma_I H''$ and $d_J = -2[(2J-1)(2J+3)]^{-1}$.

The relaxation times are related to the Bloom–Oppenheim relaxation rates by [10]

$$(\tau_{JJ'}^{\prime})^{-1} = -[J'(J'+1)/J(J+1)]^{1/2} B_1(J', J). \quad (10)$$

and

$$(\tau_{JJ'}^{\prime\prime})^{-1} = -[J'(J'+1)d_J/J(J+1)d_{J'}]^{1/2} B_2(J', J). \quad (11)$$

Moreover, $B_i(J'J)$ can be written in terms of two parameters [7] $Q_2(11)$ and R which result from the use of P_2 and quadrupole anisotropic intermolecular potential. The values $Q_2(11)$ and R are known for H₂ from experiment [7].

The exact solution of the set of coupled equations (1)–(8) gives the relaxation of the magnetization due to the spin–rotation and dipole–dipole mechanisms. Choosing the initial conditions to be $b_1(0) = 1$, and $\Upsilon_{pq}^J(0) = G_{pq}^J(0) = 0$, and then writing eqs. (1)–(8) in matrix notation,

$$\partial \mathbf{A} / \partial t = -\mathbf{R} \cdot \mathbf{A}. \quad (12)$$

it is a simple matter to solve for the time dependence

at $b_1(t)$. The vector A and the matrix R can be identified from eqs. (1)–(8).

For the two-level, $J=1$ and 3, H₂ case, the 13×13 relaxation matrix can be solved exactly. The resulting time dependence of $b_1(t)$ is given by

$$b_1(t) = \sum_{i=1}^{13} J^{(i)} \exp(-\lambda_i t). \quad (13)$$

Here $J^{(i)}$ are the weights obtained from the diagonalization procedure of the equations and are given by [1]

$$J^{(i)} = (\mathbf{T})_{1i} (\mathbf{T}^{-1})_{i1}, \quad (14)$$

where \mathbf{T} is the matrix of eigenvectors which diagonalizes R . The numerical solutions of these equations are given in the next section.

In this work, a detailed discussion of the physical meaning of the different roots is omitted. This is because they have been described elsewhere for a simple system [1] (single level spin–rotation mechanism) and, apart from arithmetical complexity here, the physical interpretation is essentially the same. However, the connection to the high density Bloom–Oppenheim theory is made in the appendix for completeness.

It is apparent, therefore, that the weak coupling limit of the set of equations (1)–(8) describing the full time behaviour of $b_1(t)$ is the same as the 2-level Bloom–Oppenheim theory. It is stressed that the weak coupling approximations eqs. (A1 and A2) are *not* invoked in the following section. Rather the full set of relaxation equations (1)–(8) is solved.

3. Numerical results

The numerical data for H₂ is given in table 1. The Larmour frequency of 61 MHz was chosen to agree with that of Armstrong's experiment [7]. The value of $Q_2(11)$ in table 1 is proportional to the density ρ in amagats[‡]. A temperature of 300 K is used and so only rotational levels $J=1$ and 3 are retained. The various relaxation rates are related to R and $Q_2(11)$ as follows [8,10]

[‡] We note that in ref. [7], $Q_2(11)$ is given in s⁻¹. It is assumed that this value is obtained at one amagat density. Moreover, for the relaxation rate to have the correct units of rad/s, it is necessary that $Q_2(11)$ have the units of rad/s, also.

Table 1
Numerical data used for H₂

ν_I (MHz) ^a	61.000
ν_J (MHz) ^b	7.250
H' (G) ^a	26.752
H'' (G) ^a	33.862
B (MHz) ^c	1.78×10^6
$Q_2(11)$ (rad μ s ⁻¹) ^a	330ρ
R^a	1.75

^a) Ref. [7]. ^b) Ref. [6]. ^c) Ref. [12].

$$(\tau'_{11})^{-1} = \left(\frac{3}{2} + \frac{3}{7} \alpha R\right) Q_2(11), \quad (15)$$

$$(\tau'_{13})^{-1} = -\left(\frac{6}{7} \alpha R\right) Q_2(11),$$

$$(\tau'_{31})^{-1} = -\left(\frac{1}{7} R\right) Q_2(11), \quad (16)$$

$$(\tau'_{33})^{-1} = \left(\frac{1}{6} + \frac{3}{7} R\right) Q_2(11),$$

and

$$(\tau''_{11})^{-1} = \left(\frac{9}{10} + \frac{3}{7} \alpha R\right) Q_2(11), \quad (17)$$

$$(\tau''_{13})^{-1} = -\left(\frac{64}{35} \alpha R\right) Q_2(11),$$

$$(\tau''_{31})^{-1} = -\left(\frac{1}{35} R\right) Q_2(11), \quad (18)$$

$$(\tau''_{33})^{-1} = \left(\frac{41}{90} + \frac{3}{7} R\right) Q_2(11),$$

where $\alpha = P_3/P_1$ and

$$P_J = (2J+1)Z^{-1} \exp[-J(J+1)B/kT], \quad (19)$$

is the Boltzmann weight in terms of the rotational constant B and the partition function Z . Using these experimentally known parameters, the coupled equations were solved, and the solution takes the form of eq. (13).

First the high density limit was checked. The values in table 2 are those calculated from the full solution at 10, 1, 0.2 and 0.05 amagats. In this regime the decay is exponential and T_2 well defined. These values agree very well with the experimental values and with those calculated based upon the Bloom–Oppenheim theory by Armstrong and Kalechstein [7]. This confirms that the high density limit of the treatment here is correct.

Fig. 1 presents the time dependence of the magnetization in the rotating frame

$$\hat{b}_1(t) = \exp(-i\omega_I t) b_1(t), \quad (20)$$

at various densities. The decay is exponential to a good approximation at a pressure of 0.05 amagats. This is the lowest pressure at which T_2 has been measured. The

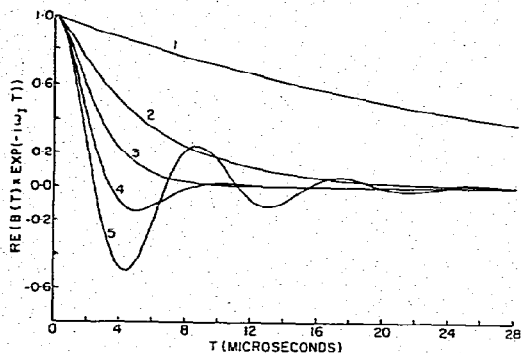


Fig. 1. Theoretical time dependence of $\hat{b}_1(t)$ at various densities (in amagats): (1) 0.050; (2) 0.010; (3) 0.005; (4) 0.0025; and (5), 0.001.

deviation from exponential decay is only visible in the very short time domain for this curve (initial slip regime [3]) or equivalently as a non-lorentzian in the far wings of the line. Non-lorentzian behaviour is observed below 0.01 amagats.

The frequency domain is more interesting. This shows in fig. 2 the same five densities as fig. 1 but centered about the various resonances. From eqs. (1)–(8) these resonances occur about ν_I , ν_J , $|2\nu_J - \nu_I|$ and $2\nu_I - \nu_J$. The main resonance is at $\nu_I = 61$ MHz. This dies with decreasing pressures, while δ , a frequency shift depending on the coupling strength, becomes independent of density at low density [1,3]. The plots in fig. 2 are obtained simply by taking the real part of the inverse Fourier transform of eq. (13),

$$I_+(\omega) = \text{Re} \sum_{i=1}^{13} J^{(i)} \frac{1}{(i\omega + \lambda_i)} \quad (21)$$

Each resonance off the ν_I resonance represents the precession of the different "lattice" modes (G_{pq}^J , Υ_{pq}^J) which are pumped by the initial magnetization $b_1(0)$. Note that G_{2-1}^J precesses in the opposite direction to the other modes. The relative intensities give the fraction of the initial magnetization which has passed to these modes.

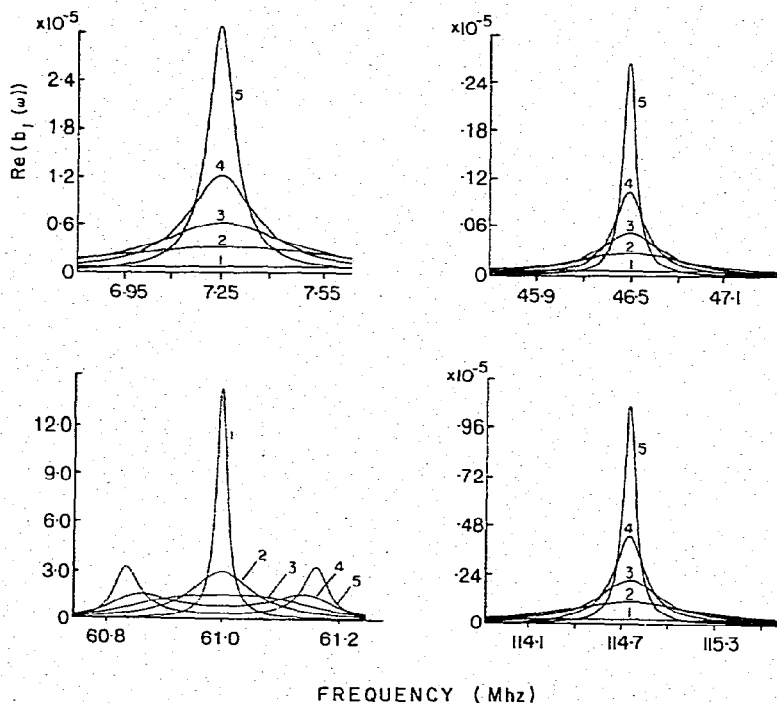


Fig. 2. Theoretical spectrum in the frequency domain at ν_I , $|2\nu_J - \nu_I|$, ν_I and $2\nu_I - \nu_J$ at the same densities as in fig. 1.

4. Suggestions for detection

In fig. 2, it is seen that the Bloch mode (the 61 MHz peak) has dropped in intensity considerably at low density and the intensity passes mostly into the two peaks centered about ν_1 . These peaks increase with decreasing density, as do the resonances at the other positions. However, as it might be difficult to resolve the two peaks at 61 MHz, it may be possible to detect the presence of a non-zero signal at these other positions after exciting the ν_J mode. Any detection of a signal would confirm the non-exponential behaviour. This detection is not expected to be easy because the total magnetization decreases with density. In fact the intensities in all the peaks are proportional to the total magnetization $b_1(0)$ at each density. At lower densities, $b_1(0)$ decreases. On the other hand, at lower densities, the non-Bloch modes become sharper, which favours detection [11] if enough signal is present.

From fig. 2 it is clear that an experiment at 0.05 amagats would appear exponential thus confirming Armstrong's experiment [7]. In fact, even at 0.005 amagats detection of the non-Lorentzian behaviour at 61 MHz may be difficult (see fig. 2). Hence it appears that under present experimental restrictions, the only way to test this theory is to look for signals at this pressure at ν_J , $|2\nu_J - \nu_1|$ or $2\nu_J - \nu_J$. Moreover, a lower applied field (but still in the Paschen-Back regime) increases the transfer of polarization to these other modes and favours detection [5].

Table 2

Comparison between experimental [7] and theoretically calculated value of T_2 at five densities at 300 K and $\nu_J = 61$ MHz. Below 0.01 amagats T_2 can no longer be defined. However, a relaxation time can be estimated as in ref. [1], and these are given for three densities

T_2 ($\mu\text{s}/\text{rad}$)		Density (amagat)
exp.	theory	
1060	1080	10
166	170	1
56	54.9	0.2
14	14.3	0.05
	2.48	0.01
	1.3	0.005
	2.6	0.0025
	6.3	0.001

5. Discussion

In this paper, using no adjustable parameters, the exact low density relaxation of the nuclear magnetic relaxation of H₂ has been treated. Both a spin-rotation and dipole-dipole mechanism are included and the two rotational levels, $J=1$ and 3, retained. The results differ from ref. [4] where a single relaxation time is used. While ref. [4] studied only those peaks about ν_J , this paper predicts, in the low density limit, other resonances caused by the coupling of nuclear spin rotational modes. Experimental detection of these new resonances would provide a possible alternate means for confirmation of the predicted breakdown of the Bloch description, and the presence of non-exponential behaviour.

On the other hand a variety of experiments can be envisaged in the low density regime. For example, the system can be pumped at ν_J and effects looked for at ν_J . This is equivalent to an Overhauser type experiment, but between the rotational and nuclear Zeeman levels. At low densities, this is feasible since relaxation of the rotational levels is less efficient than coupling to the nuclear spin modes. The only difference between the calculation of this effect and that presented in section 3 would be to change the initial conditions from $b_1(0) = 1$, $\Upsilon_{pq}^J = G_{pq}^J = 0$ to $b_1(0) = 0$ and $\Upsilon_{pq}^J = G_{pq}^J \neq 0$.

The results here are of interest theoretically since they give a clear example of the breakdown of the usual macroscopic theories. The effects are expected to be typical. Moreover, as recently shown the breakdown is well described by existing statistical mechanical theories [3] and give a well defined recipe for studying other systems which contain either strong coupling, or measurable transient effects. Finally, the calculation here for H₂ indicates that the effects of non-exponentiality, due to a breakdown of a weak spin-lattice coupling approximation, are very small. Hence for standard NMR experiments the usual theories [6,9,10] can be said to give an excellent description of the relaxation.

Appendix

In this appendix, it is shown that eqs. (1)–(8) reduce to the usual expressions for T_2^{-1} in the weak

coupling limit. This can be done by treating c and c_d , in the sets of coupled equations, as perturbation parameters and finding the smallest eigenvalue for each case. Equivalently, one can cast the matrix of differential equations into an integral equation [1] and solve the resulting memory equation in the markovian approximation. Finally one can invoke the rotating frame approximation [10,5] which is equivalent to both the above limits. In each case, the Bloom–Oppenheim [7,9] expressions for the transverse relaxation rates $(1/T_2)_{sr}$ and $(1/T_2)_{dd}$ are obtained. Here we use the rotating frame approximation. Namely, we assume that the modes Υ_{pq}^J and G_{pq}^J are "in phase" with the nuclear Larmor precession so the time dependence of Υ_{pq}^J and G_{pq}^J is approximately given by

$$\partial \Upsilon_{pq}^J / \partial t \approx i\omega_I(p+q)\Upsilon_{pq}^J, \quad (\text{A.1})$$

$$\partial G_{pq}^J / \partial t \approx i\omega_I(p+q)G_{pq}^J. \quad (\text{A.2})$$

The single J level case is treated first. Hence it is assumed that $1/\tau_{JJ'} = 0$ for $J \neq J'$ for now. Then, substituting eq. (A.1) into eqs. (2) and (3) one obtains

$$\Upsilon_{10}^J \approx c\tau_{JJ}^J b_1, \quad (\text{A.3})$$

$$\Upsilon_{01}^J \approx -[i(\omega_I - \omega_J) + 1/\tau_{JJ}^J]^{-1} c b_1, \quad (\text{A.4})$$

while from substituting eq. (A.2) into eqs. (5)–(8), the approximations to G_{pq}^J are,

$$G_{10}^J \approx +[i(\omega_I - \omega_J) + 1/\tau_{JJ}^J]^{-1} c_d d_J \sqrt{3} b_1, \quad (\text{A.5})$$

$$G_{01}^J \approx -\tau_{JJ}^J c_d d_J \sqrt{3}/2 b_1, \quad (\text{A.6})$$

$$G_{-12}^J \approx [-i(\omega_I - \omega_J) + 1/\tau_{JJ}^J]^{-1} c_d d_J / \sqrt{2} b_1. \quad (\text{A.7})$$

$$G_{2-1}^J \approx -[2i(\omega_I - \omega_J) + 1/\tau_{JJ}^J]^{-1} c_d d_J / \sqrt{2} b_1. \quad (\text{A.8})$$

Substitution of eqs. (A.3) and (A.4) into eq. (1) gives $db_1/dt = i\omega_I(1 - \sigma_J^{sr})b_1 - (1/T_2)_J^{sr} b_1$, (A.9)

where T_2^{-1} is identified as

$$(1/T_2)_J^{sr} \equiv \frac{1}{3} J(J+1)\gamma^2 (H')^2 \times \left[\tau_{JJ}^J + \frac{\tau_{JJ}^J}{1 + (\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2} \right], \quad (\text{A.10})$$

and the chemical shift is

$$\sigma_J^{sr} \equiv \frac{1}{3} \frac{J(J+1)\gamma^2 (H')^2 (\omega_I - \omega_J) (\tau_{JJ}^J)^2}{\omega_I [1 + (\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2]}. \quad (\text{A.11})$$

Repeating the identical procedure for the dipolar case, eqs. [(A.5)–(A.8)] in eq. (4) leads to

$$(1/T_2)_J^{dd} = \frac{3J(J+1)\gamma_I^2 H''^2}{5(2J-1)(2J+3)} \times \left[3\tau_{JJ}^J + \frac{5\tau''}{1 + (\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2} + \frac{2\tau''}{1 + 4(\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2} \right], \quad (\text{A.12})$$

and

$$\sigma_J^{dd} = -\frac{3J(J+1)\gamma_I^2 H''^2}{5(2J-1)(2J+3)\omega_I} \times \left[\frac{(\omega_I - \omega_J) (\tau_{JJ}^J)^2}{1 + (\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2} + \frac{4(\omega_I - \omega_J) (\tau_{JJ}^J)^2}{1 + 4(\omega_I - \omega_J)^2 (\tau_{JJ}^J)^2} \right]. \quad (\text{A.13})$$

For the multilevel case, with $1/\tau_{JJ'} \neq 0$, it is seen that eqs. (2) and (3) and (5)–(8) contain a matrix of relaxation times and each equation actually corresponds to a set of collisionally coupled equations. Each of these can be diagonalized by standard procedures. For the two-level case [9,10] which is applicable to H_2 gas, eqs. (2) and (3) and (5)–(8) correspond to six sets of two coupled equations. For example, using the rotating frame approximation, eq. (A.2), one of the set, eq. (5), becomes

$$c_d d_J (\sqrt{3}/2) b_1 \approx +i(\omega_I - \omega_J) G_{10}^J + \sum_{\substack{J'=1 \\ \text{odd}}} G_{10}^{J'} / \tau_{JJ'}^J, \quad (\text{A.14})$$

with $J = 1$ and 3. These two equations can be diagonalized by writing,

$$X_{10}^1 = \cos \theta G_{10}^1 + \sin \theta G_{10}^3, \quad (\text{A.15})$$

$$X_{10}^2 = -\sin \theta G_{10}^1 + \cos \theta G_{10}^3, \quad (\text{A.16})$$

and introducing

$$D_1 \equiv \cos \theta d_1 + \sin \theta d_3, \quad (\text{A.17})$$

$$D_2 \equiv -\sin \theta d_1 + \cos \theta d_3. \quad (\text{A.18})$$

The value of θ and the eigenvalues are found from

$$\begin{pmatrix} 1/\tau''_{11} & 1/\tau''_{13} \\ 1/\tau''_{31} & 1/\tau''_{33} \end{pmatrix} X_{10}^\alpha = \Lambda_{2\alpha} X_{10}^\alpha \quad (\text{A.19})$$

It follows that, [cf. eq. (A.5)]

$$X_{10}^\alpha \approx [i(\omega_I - \omega_J) + \Lambda_{2\alpha}]^{-1} c_d D_\alpha (\sqrt{3}/2) b_1, \quad (\text{A.20})$$

from which G_{10}^J , $J = 1, 3$, can be obtained. This procedure can be applied to eqs. (2) and (3), the rotating frame approximation invoked, and the results substituted into eqs. (1) and (4). This gives the analogous equations to (A.10) and (A.12) which are identical to the first two equations in ref. [7].

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