

Non-Lorentzian NMR spectra at low densities

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When the weak coupling approximation is not applicable to the derivation of nuclear magnetic relaxation rates, the transverse and longitudinal components of the magnetization decay nonexponentially. In this paper, the frequency domain is studied for a typical case of gases at low density. This example illustrates the non-Lorentzian behavior expected and gives a clear realization of the rotating frame approximation.

I. INTRODUCTION

In a recent paper¹ by one of us the breakdown of the Bloch equations for gases at low densities was studied by evaluating the exact time dependence of the nuclear magnetization for a simple model. This model is a single spin 1/2 relaxing via a spin rotation intramolecular mechanism. For illustrative purposes, numerical data was chosen to be typical for H₂. The results are not definitive for H₂, however, since the dipole mechanism is ignored for mathematical ease. It was shown that as the density decreases (and the correlation time increases) the weak coupling and "Markovian" approximations, commonly used in deriving the Bloch equation, begin to break down. When the collision frequency is of the same order of magnitude as, or smaller than, the intramolecular coupling strength, the relaxation is nonexponential and a T₂ cannot be defined. As the correlation time continues to increase, the time dependence of the magnetization displays a superposition of damped oscillations. Moreover, as the density decreases, the transverse relaxation rate first increases and then after passing through a maximum, begins to decrease. In the limit of zero density, no collisions occur and the relaxation rate goes to zero. This same problem has been discussed recently from a different point of view,² but in both treatments the unphysical result that previously existed,³ namely that the transverse relaxation rate goes to infinity at zero density, is resolved.^{3(a)}

In this paper we present the frequency domain results rather than the time domain relaxation. The reason for this is that the frequency domain dramatically illustrates the breakdown of the Bloch description and emphasizes several features which are masked in the time domain. In particular, the relaxation for a spin rotation mechanism was found in Ref. 1 to be dominated by two eigenvalues at low densities while the third made negligible contributions to the relaxation and could not be seen. Here it is shown that this third component, oscillating at ω_r rather than ω_I , grows with decreasing density.

Also it makes more of a contribution to the relaxation as the difference between the Larmor precession frequencies, ω_I and ω_r , decreases. Thus this model shows that the rotating frame approximation⁸ is obeyed. Moreover, this approximation is derived and tested numerically for the first time. It is shown that the rotating frame approximation is an excellent approximation under the assumption of weak coupling⁶ between the modes.

Another aspect which we wish to emphasize is the general nature of the effects which are illustrated by this useful mathematical model. In particular, for liquids, rather than gases, intermolecular interactions can be quite strong with the consequence that the Lorentzian line shape may be destroyed (and the relaxation becomes nonexponential) as other motions begin to couple to the nuclear spin. Experimentally, non-Lorentzian line shapes are common in microwave⁴ and ir⁵ spectroscopy, but are usually not observed in magnetic resonance spectroscopy. The calculation¹ discussed below unequivocally illustrates that non-Lorentzian NMR line shapes arise in the gas phase as the density is decreased. The type of behavior found is expected to be typical of this breakdown when other mechanisms are present.

For mathematical ease, only the spin rotation mechanism is included, but quantitative calculations can easily be performed for other mechanisms if the density regime is experimentally accessible and if there is interest to study it.^{5(a)} Moreover the spin rotation is a mechanism present in many spin systems.

II. THE NMR SPECTRUM

The spin rotation, single correlation time model is described elsewhere.^{1,2,6,7} For this model the memory kernel $K_1(t)$ for the transverse magnetic component can be obtained explicitly and the solution obtained in the time domain or frequency domain. Here the frequency spectrum is examined,⁷

$$\hat{b}_1(\omega) = J(\omega)b_1(0) = \frac{[1 + i(\omega - \omega_r)\tau'] [1 + i(\omega - \omega_I)\tau'] b_1(0)}{i(\omega - \omega_I) [1 + i(\omega - \omega_r)\tau'] [1 + i(\omega - \omega_I)\tau'] + 1/3 c^2 J(J+1)\tau' [2 + i(2\omega - \omega_I - \omega_r)\tau']}, \quad (1)$$

where ω is the applied frequency; ω_I and ω_r are the nuclear and rotational Larmor frequencies, respectively; τ' is the rotational correlation time and $\hat{b}_1(\omega)$ is the Fourier transform of the transverse nuclear magnetic

polarization with initial condition $b_1(0)$. The spin rotation coupling constant is c .

Using the same values as in Ref. 1, namely $J=1$, ω_I

= 61 MHz, $\omega_J = 7.25$ MHz, $c = 0.115$ MHz, and $\tau' = 8 \times 10^{-8}$ psec, the real part of the spectrum is calculated. This is plotted for various pressures (p in torr) in Fig. 1. For pressures $p = 0.02$ torr and greater, there is one peak centered at 61 MHz and this is given to an excellent approximation by the Lorentzian:

$$\text{Re}J(\omega) = \frac{T_2}{1 + (\omega - \omega_J)^2 T_2^2}, \quad (2)$$

where³

$$T_2^{-1} = \frac{1}{3} c^2 J(J+1) \left[\tau' + \frac{\tau'}{1 + (\omega_J - \omega_J)^2 \tau'^2} \right]. \quad (3)$$

As the density decreases, and τ' increases, the line broadens and becomes non-Lorentzian. Finally at lower densities the central peak separates into two peaks equally spaced about ω_J . At the same time, a very small peak grows about the rotational Larmor frequency at $\omega_J = 7.25$ MHz. The scale of this peak is 10^{-6} that of the ones at 61 MHz. (See Fig. 1.)

It is clear that for this example, the relaxation rate (proportional to the linewidth) first increases and then decreases with decreasing pressure. Therefore the relaxation rate passes through a maximum as a function of pressure. Also it is clear from Fig. 1 that a single relaxation time, namely T_2 , loses meaning for the broadest peak since the line shape is non-Lorentzian. This confirms the earlier conclusion¹ that T_2 is not defined in the regime of fastest relaxation.

The mathematical form for the spectral density is the Fourier transform of the time dependence. The exact time dependence in this model is governed by three differential equations,^{1,7}

$$\frac{\partial b_1(t)}{\partial t} = i\omega_J b_1(t) + \frac{1}{3} cJ(J+1)(T_{01} - T_{10}), \quad (4)$$

$$\frac{\partial T_{10}}{\partial t} = i\omega_J T_{10} + c b_1(t) - T_{10}/\tau', \quad (5)$$

$$\frac{\partial T_{01}}{\partial t} = i\omega_J T_{01} - c b_1(t) - T_{01}/\tau'. \quad (6)$$

The exact time domain solution to these equations with initial conditions $b_1(0)$, and $T_{10}(0) = T_{01}(0) = 0$ is determined by the three characteristic roots λ_α . For the transverse magnetization, $b_1(t)$, the exact solution to the above set of equations is

$$b_1(t) = \sum_{\alpha=1}^3 \exp(-\lambda_\alpha t) J_{11}^{(\alpha)} b_1(0), \quad (7)$$

while Eq. (1) gives the frequency domain solution, being the Fourier transform of Eq. (7). For the case of weak coupling, the three residues⁷ are $J_{11}^{(1)} \approx 1$, $J_{11}^{(2)} \approx J_{11}^{(3)} \approx 0$ when $c^2 \tau'^2 \ll 1$. In this case the spectrum is given by Eq. (2) with $1/T_2$ given by Eq. (3).

For strong coupling, when $c^2 \tau'^2 > 1$, the frequency spectrum is given by,⁷ ($\omega_I \neq \omega_J$)

$$\hat{b}_1(\omega) \approx \frac{\tau'}{1 + 4(\omega - \omega_I - \delta)^2 \tau'^2} + \frac{\tau'}{1 + 4(\omega - \omega_I + \delta)^2 \tau'^2} + \frac{1}{3} \frac{c^2 J(J+1)}{(\omega_I - \omega_J)^2} \frac{\tau'^2}{1 + (\omega - \omega_J)^2 \tau'^2}, \quad (8)$$

with $\delta \approx [1/3J(J+1)]^{1/2} c$, and $b_1(0) = 1$.

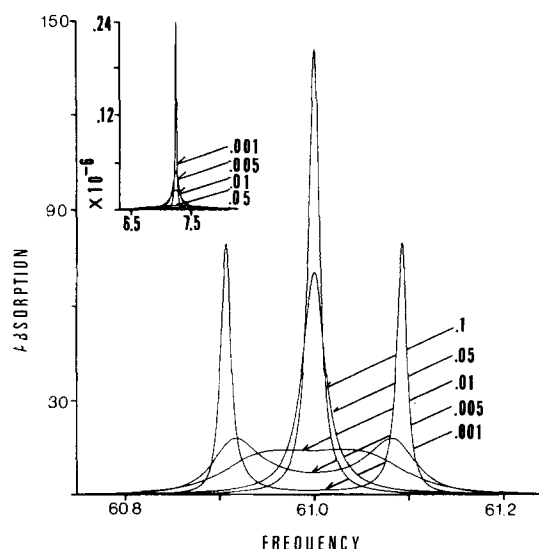


FIG. 1. Absorption spectrum in arbitrary units of the transverse component of a single spin relaxing via a spin rotation mechanism as a function of frequency in MHz for different pressure in torr.

III. THE ROTATING FRAME APPROXIMATION

Equation (8) is a good approximation to the lowest density curves in Fig. 1. It also dramatically illustrates and confirms an approximation which has been exploited in NMR theory⁸ and which is quite general in nature.⁶ That is, only those components which are oscillating in phase with the observable of interest need be retained. In the model studied here, the component oscillating at ω_J makes negligible contribution to the relaxation of a nuclear spin oscillating at $\omega_J \gg \omega_I$. If ω_J is increased, then the ω_J component makes more of a contribution. [This is shown in Fig. 2 for $\omega_I = 61$ MHz and for $\omega_J = 60.75$ MHz.] Hence the time dependence of an observable can be written as a sum of exponentials as Eq. (7) but to an excellent approximation, the sum need extend over only those modes which are oscillating in phase with the frequency of the observable of interest.

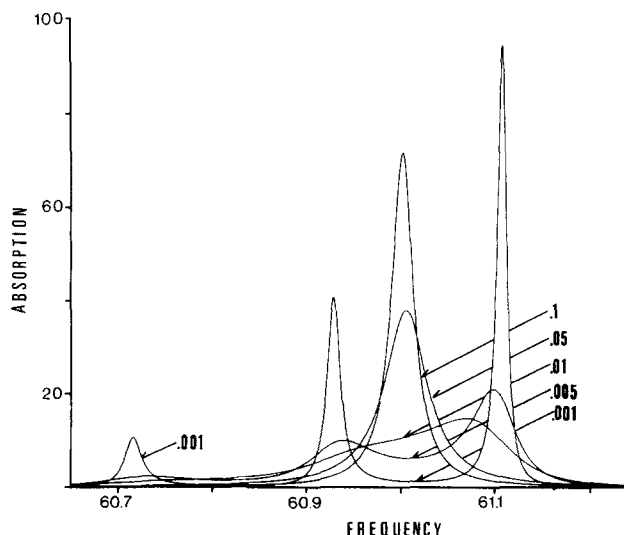


FIG. 2. Same as Fig. 1, but for $\omega_J = 60.75$ MHz.

If, in addition, there is weak coupling present so that the observable of interest [e.g., $b_1(t)$] decays much more slowly than the other modes of the system, Υ_{kl} , then the time dependence of all the irrelevant modes is particularly simple. Referring to Eq. (22) of Ref. (1), it is seen that the time dependence of $\Upsilon_{10}(t)$ and $\Upsilon_{01}(t)$ are both determined by the same characteristic roots as given for the transverse magnetization, Eq. (7), but with different residues. However in contrast, $\Upsilon_{10}(t)$ and $\Upsilon_{01}(t)$ are microscopic observables and relax on the τ' time scale whereas $b_1(t)$ is only of interest in the long time (experimentally accessible) domain. Thus, only the long time contributions to $\Upsilon_{10}(t)$ and $\Upsilon_{01}(t)$ are important for determining $b_1(t)$. These are

$$\begin{aligned} \Upsilon_{10}(t) &\cong -\Upsilon_{01}(t) \cong c\tau' e^{i\omega_I t} e^{-t/T_2} b_1(0) \\ &\cong c\tau' b_1(t), \end{aligned} \quad (9)$$

where initial slips⁷ have been ignored and for convenience the extreme narrowing limit, $(\omega_I - \omega_J)\tau' \ll 1$, is invoked.

Substitution of Eq. (9) into Eq. (4) results in the usual expression for T_2^{-1} , Eq. (3). Certainly, keeping the other roots in Eq. (9) makes only transient contributions to the relaxation.

Differentiating Eq. (9) gives

$$\frac{\partial \Upsilon_{kl}(t)}{\partial t} \cong \left(i\omega_I - \frac{1}{T_2} \right) \Upsilon_{kl}(t), \quad k+l=1, \quad (10)$$

which can be compared to Eqs. (5) and (6). It is seen that because $T_2^{-1} \ll \tau'^{-1}$ the Υ_{kl} , being microscopic, relax on the time scale of τ' and not T_2 . Hence Eq. (10) is given to an excellent approximation in the weak coupling regime by

$$\frac{\partial \Upsilon_{kl}(t)}{\partial t} \cong i\omega_I \Upsilon_{kl}(t), \quad k+l=1. \quad (11)$$

Physically, Eq. (11) states that the only components of Υ_{10} and Υ_{01} which are important to the relaxation of the magnetization are those which are in phase⁸ with the precession of the magnetization. Alternatively, Eq. (11) can be viewed as a consequence of the nonequilibrium magnetization driving the microscopic degrees of freedom out of equilibrium. In the weak coupling regime, these modes are predominantly in phase with the precession of the magnetization.

Equation (11) is obtained here by considering an approximation to a known exact solution for a particular model. In most cases the exact solution is not available and one is faced with the problem of solving a set of coupled differential equations. Equation (11) can be used to simplify these by retaining only those parts which determine the long time dependence. This approach should be particularly useful for treating the relaxation equations for systems of spins which have different chemical shifts.

Use of the rotating frame approximation enables the three differential equations, Eqs. (4) to (6) to be solved very simply for $b_1(t)$.

ACKNOWLEDGMENT

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¹B. C. Sanctuary, *J. Chem. Phys.* **67**, 4511 (1977).

²G. Tenti and F. R. McCourt, *J. Chem. Phys.* **65**, 623 (1976).

³A. Abragam, *The Principles of Nuclear Magnetization*, (Oxford University, London, 1961).

^{3(a)}Note added in proof: We note that recently F. R. McCourt and G. Tenti [*Chem. Phys.* **32**, 23 (1978)] have studied the frequency domain for a similar case to that treated here. Apart from the inconsequential use of different numerical constants, the results differ in that the third mode, which appears at low densities at ω_J is not included by McCourt and Tenti.

⁴C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, (McGraw-Hill, New York, 1955).

⁵G. Herzberg, *Infrared and Raman Spectra*, (Van Nostrand Reinhold, New York, 1945).

^{5(a)}Note added in proof: Since going to press, R. L. Armstrong and W. Kalechstein [*Chem. Phys.* **28**, 125 (1978)] have attempted to observe the non-Lorentzian behavior at low densities. Although unsuccessful, their careful experiments are encouraging that these small effects may eventually be seen.

⁶B. C. Sanctuary and R. F. Snider, *Can. J. Phys.* **53**, 707 (1975).

⁷B. C. Sanctuary and R. F. Snider, *J. Chem. Phys.* **67**, 5517 (1977).

⁸F. M. Chen and R. F. Snider, *J. Chem. Phys.* **48**, 3185 (1968).