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Nuclear-Spin Relaxation in Low-Density Molecular Hydrogen at Room Temperature*

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All theoretical approaches to the problem of nuclear-spin relaxation in molecular hydrogen attempt to obtain expressions for the macroscopic longitudinal and transverse relaxation times T_1 and T_2 from microscopic equations governing the relaxation processes. Recently McCourt and Moraal¹ have presented such a derivation based on the Waldmann-Snyder kinetic equation. The conversion of the microscopic kinetic equation to a set of macroscopic equations is achieved through the formation of three moment equations.² For a single-level system it is then a straightforward matter to complete the solution of the moment equations to obtain the Bloch equation. Molecular hydrogen at 77 K provides an example of such a system since essentially all of the ortho molecules are in the $j=1$ rotational state. A comparison of the experimental measurements of Hardy³ for $n\text{-H}_2$ at 77 K shows that theory and experiment are in good agreement for T_2 and in reasonable agreement for T_1 .

For a multilevel system, however, before it is possible to complete the solution of the moment equations to obtain the Bloch equation it is necessary to give careful consideration to the role played by energetically inelastic collisions. Several different cases can be distinguished.

Case I. If there are no energetically inelastic

collisions then each j state acts independently in the relaxation process and separate relaxation rates may be associated with each rotational level. The measured relaxation rates will then be obtained as a Boltzmann average of the relaxation rates describing the individual levels. In particular,

$$T_1^{-1} = \sum_j p_j (T_1^{-1})_j \\ = \frac{2}{3} c^2 \left\langle \frac{j(j+1)\tau'_j}{1 + \omega^2 \tau'^2_j} \right\rangle_0 + \frac{2}{75} (2I+3)(2I-1) \\ \times d^2 a_I^2 \left\langle \frac{j(j+1)}{(2j-1)(2j+3)} \tau''_j \left(\frac{1}{1 + \omega^2 \tau''^2_j} + \frac{4}{1 + 4\omega^2 \tau''^2_j} \right) \right\rangle_0, \quad (1)$$

where c and d are the spin-rotation and dipolar coupling constants, $I=1$ is the total nuclear spin of an ortho-hydrogen molecule, $a_{I=1} = \frac{1}{2}$,⁴ $\omega = \omega_I - \omega_J$ with ω_I and ω_J the nuclear and rotational Larmor frequencies, and τ'_j and τ''_j are the correlation times for level j associated with the spin rotation and dipolar interactions. This corresponds to the procedure given by Freed,⁵ Bloom *et al.*,⁶ and Chen and Snyder.⁴

Case II. If the number of energetically inelastic collisions is large enough so that on the time scale

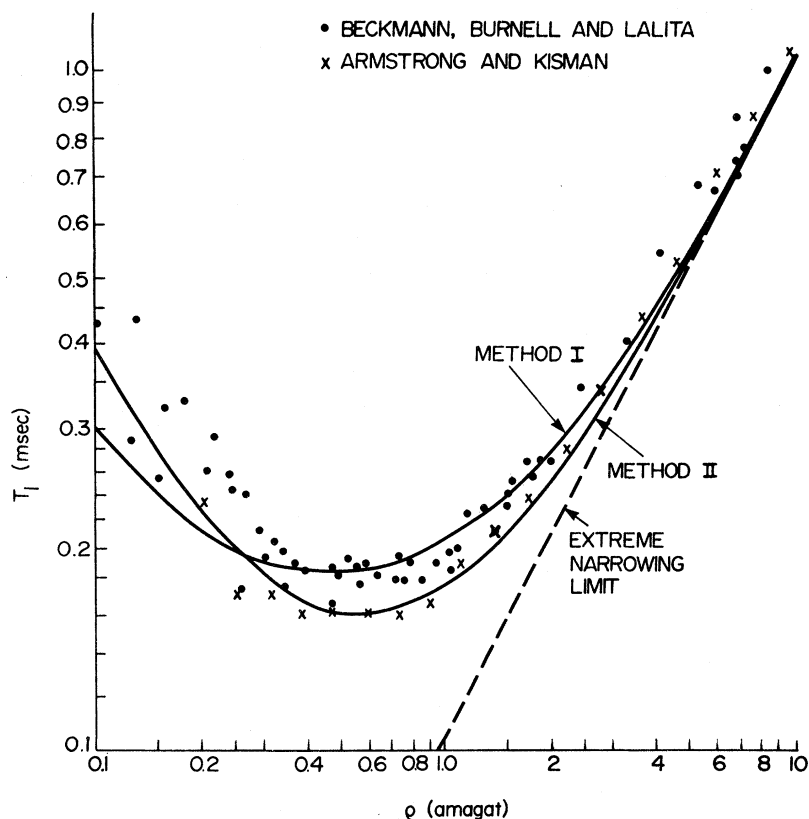


FIG. 1. Density dependence of T_1 as measured in $n\text{-H}_2$ at 298 K. The solid curves are theoretical calculations, for a resonance frequency of 30 MHz, based on two different methods of averaging over the rotational states. The points indicated by the closed circles were obtained at 30 MHz and those indicated by the \times 's at 28 MHz.

of the nuclear-spin relaxation experiment an ortho molecule may not be associated with a unique j state, but still small enough so that they make no significant contribution to the collision integrals, then correlation times which are Boltzmann averages of the correlation times associated with specific rotational states should be taken. That is,

$$\begin{aligned} (\tau'_{av})^{-1} &= \sum_j p_j (\tau'_j)^{-1} = \sum_j p_j [j(j+1)]^{-1} (\omega'_{co11})^j, \\ (\tau''_{av})^{-1} &= \sum_j p_j (\tau''_j)^{-1} \\ &= \sum_j p_j [j(j+1)(2j-1)(2j+3)]^{-1} (\omega''_{co11})^j, \end{aligned}$$

where $(\omega'_{co11})^j$ and $(\omega''_{co11})^j$ are the collision frequencies for state j associated with the spin-rotation and dipolar interactions as deduced neglecting inelastic collisions. In this case,

$$\begin{aligned} T_1^{-1} &= \frac{2}{3} c^2 \langle j(j+1) \rangle_0 \frac{\tau'_{av}}{1 + \omega'^2 (\tau'_{av})^2} + \frac{2}{75} (2I+3)(2I-1) d^2 a_I^2 \\ &\times \left\langle \frac{j(j+1)}{(2j-1)(2j+3)} \right\rangle_0 \tau''_{av} \left(\frac{1}{1 + \omega''^2 (\tau''_{av})^2} + \frac{4}{1 + 4\omega''^2 (\tau''_{av})^2} \right). \end{aligned} \quad (2)$$

Case III. If energetically inelastic collisions occur at least as frequently as elastic collisions then the j -dependent moment equations should be averaged over the j distribution at once to give moment equations for the bulk magnetizations in the gas. That is, the j states are sufficiently

strongly coupled by collisions that the average correlation times are given by

$$\begin{aligned} (\tau'_{av})^{-1} &= \frac{\langle (\omega'_{co11})_j \rangle_0}{\langle j(j+1) \rangle_0}, \\ (\tau''_{av})^{-1} &= \frac{\langle (\omega''_{co11})_j \rangle_0}{\langle j(j+1)(2j-1)(2j+3) \rangle_0}. \end{aligned}$$

The relaxation rate is determined by the substitution of these expressions into (2). This corresponds to the procedure used by McCourt and Moraal.¹

For molecular hydrogen at room temperature it should be sufficient to include in addition to the $j=1$ level, the $j=3$ and $j=5$ rotational levels. It is known from acoustical measurements^{7,8} that of the order of 1 in 300 collisions are energetically inelastic. This result implies that the contributions to collision cross sections from inelastic collisions will be less than 1%. However, at 1 atm pressure, of the order of 10^7 collisions occur each second which mix the rotational states. Therefore, on the time scale of a nuclear-spin relaxation experiment ($\sim 10^{-4}$ sec), of the order of 10^3 inelastic collisions occur. The obvious conclusion is that the averaging procedure corresponding to case (II) is to be expected experimentally.

Measurements of T_1 through the region of the T_1 minimum in $n\text{-H}_2$ at 298 K at 30 and 28 MHz have been carried out at the University of British Columbia and the University of Toronto, respectively. The experimental techniques employed have been discussed elsewhere.^{9,10} The data obtained are shown in Fig. 1. Those points indicated by the symbol \times represent averages of at least three data points and have an associated statistical error of $\sim \pm 5\%$. The points indicated by the closed circle correspond to individual determinations. In the vicinity of the minimum the data represented by the \times 's are significantly lower than the data indicated by the closed circles. This difference reflects in part the effect of the use of different frequencies to obtain the two sets of data. Theoretically, it is predicted that the minimum value of T_1 for a resonance frequency of 28 MHz should be $\sim 7\%$ shorter than for a resonance frequency of 30 MHz. The residual difference can be attributed to systematic errors.

Theoretical curves were calculated using each of the three procedures outlined above using as the sole adjustable parameter the value $T_1/\rho = 0.105$ msec amagat⁻¹ in the extreme narrowing limit. The curves for cases I and II, at a resonance frequency of 30 MHz, are shown on the graph. The curve for case III lies between those for cases I and II but nearer to curve II. A perusal of the data in its entirety permits us to conclude that theory and experiment are in satisfactory agreement, but that the experiments have not been sufficiently refined to permit an unambiguous choice between the various methods of averaging. A better test of the theory must await more accurate experiments, preferably carried out at a higher temperature at which the problem of the choice of an averaging procedure becomes still more important.

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Convergence of Activity Expansions for Lattice Gases*

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A recent theorem by Ruelle is shown to be applicable to the calculation of lower bounds on the radius of convergence of activity expansions for lattice gases. Systems with nearest-neighbor repulsive interactions are used as examples. Special consideration is given to systems whose molecules possess infinitely repulsive potentials.

Systems composed of interacting molecules have played a central role in the development of statistical mechanics in spite of the fact that mathematically rigorous results for such systems are rather scarce. The compromise between resemblance to physical reality and mathematical necessity has led to the formulation of many models, some of the

most successful being those that relate to lattice statistics.

Shortly after Onsager¹ obtained the partition function for the square ferromagnetic Ising model, Lee and Yang² proved that for this model and its higher-dimensional analogs all the zeros of the partition function $P(z)$ reside on the unit circle in the complex