NUCLEAR MAGNETIC SPIN-LATTICE RELAXATION BY SPIN-ROTATIONAL INTERACTIONS*

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The possible importance, in nuclear magnetic spin-lattice relaxation, of the magnetic fields produced by molecular rotation was pointed out by Bloembergen, Purcell, and Pound[1] in their classic paper on nuclear relaxation. The purpose of this Letter is to present experimental evidence that spin-rotational interactions provide the dominant relaxation mechanism in certain molecular liquids.

Earlier work[2] on the proton and fluorine T_1's at room temperature in CH_2FCl, CHF_2Cl, $CHFCl_2$, and 1, 3, 5-trifluorobenzene demonstrated that the anisotropy in the fluorine nuclear magnetic shielding contributes an appreciable, field-dependent, term to the fluorine T_1. In these molecules, the direct dipole-dipole interactions among the nuclei are nearly identical for protons and fluorine. Moreover, because of their rigid molecular framework, the molecules should have the same correlation time τ_c governing the T_1 of fluorine nuclei as well as of protons. Therefore, even though it is difficult to make a sufficiently accurate estimate of τ_c to predict quantitative values for T_1, the ratio of the T_1's, $R = T_{1\text{H}}/T_{1\text{F}}$, should be predictable to better accuracy. However, it was found that although the predicted ratio of the dipolar contributions to T_1, R_{dip}, ranged between 0.4 and 1.0 for the four liquids, the observed ratio ranged between 1.5 and 9.2. In addition, R_{obs} increased with the applied magnetic field, indicating the presence of a field-dependent interaction which decreased the fluorine T_1 but had little or no effect upon the proton T_1.

This behavior agrees qualitatively with the effects calculated on the basis of anisotropy $\Delta\sigma$ in the chemical shift tensor σ inasmuch as the proton shifts are too small for their anisotropy to contribute much to T_1. However, even though the anisotropy is large enough to be important for fluorine, estimates of its magnitude based on chemical shift theory and also on the field dependence of R_{obs} led to the result that R_{obs} should be about 1.5 R_{dip} for T_1's at 20 Mc/sec. Therefore, it was concluded that some additional more important factor was shortening the fluorine T_1 and causing the several-fold difference[1] between R_{dip} and R_{obs}.

That this additional relaxation mechanism involves the spin-rotational interaction is shown by our subsequent measurements of the temperature dependence of the proton and fluorine T_1's. Results for CH_2FCl, CHF_2Cl, and CHF_3 are presented in Fig. 1 as a semilogarithmic plot of T_1 versus $10^3/T$°K; qualitatively similar but less extensive data have been obtained[3] for $CHFCl_2$. The increase of T_1 with temperature implies that $\omega^2\tau_c^2 \ll 1$; however, the curvature of the plots for both the proton and fluorine T_1 from straight lines at higher temperatures indicates deviations from "ideal" behavior.[1] Taken individually, such deviations for either the proton or the fluorine T_1 could be attributed to any of several aspects of the liquid-state structure or purity. The significant feature is that the deviations are larger for fluorine than for the proton; and, moreover, the differential effect is itself strongly temperature dependent. This

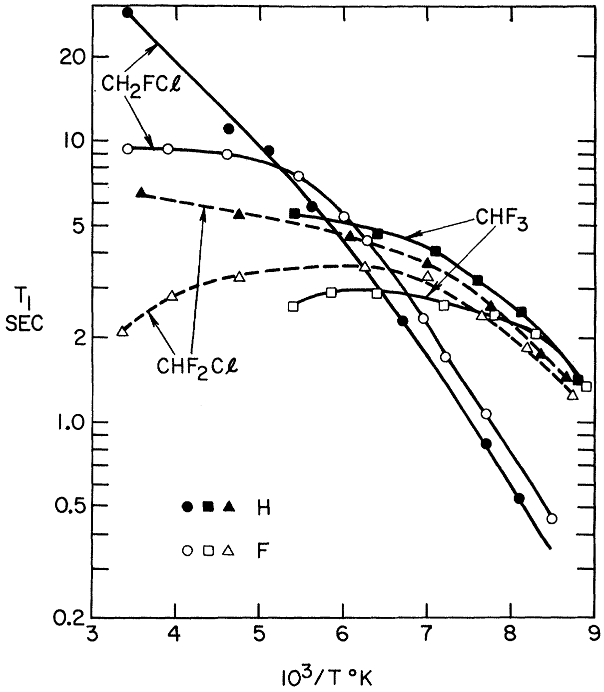

FIG. 1. The temperature dependence of the proton and fluorine T_1 observed by rf pulse methods at 20 Mc/sec in several liquid fluoromethanes.

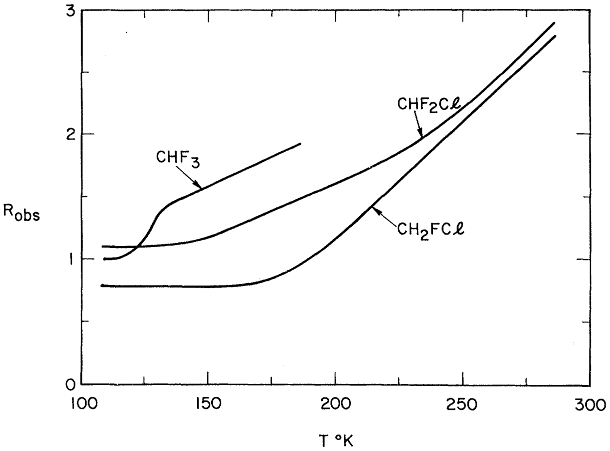

FIG. 2. The differential dependence upon temperature of the proton and fluorine T_1 in the same molecule. R_{obs} is defined as $T_{1\mathrm{H}}/T_{1\mathrm{F}}$, where the T_1's are taken from the experimental curves in Fig. 1.

may be seen in Fig. 2 when the data in Fig. 1 are replotted as R_{obs} versus T.

At low temperatures, R_{obs} approaches a constant, limiting value which is close to $1.5R_{\mathrm{dip}}$. In other words, the proton T_1 at low temperatures is that given by nuclear dipole-dipole interactions alone, while that for fluorine is determined by the nuclear dipole-dipole interaction *plus* $\Delta\sigma$. At higher temperatures R_{obs} increases, and after an intermediate curved region it becomes a linear function of the temperature. This is equivalent to stating that at higher temperatures there is an additional contribution to the fluorine T_1 such that

$$1/T_{1\mathrm{F}} \sim \tau_c(A+BT). \qquad (1)$$

The only plausible mechanism for these results appears to be the spin-rotation interaction.

First of all, the spin-rotation interaction should be small for the proton and much larger for fluorine. This is implicit in the proportionality which Ramsey[4] has pointed out between the spin-rotation constant and the second-order paramagnetic term in the nuclear magnetic shielding, inasmuch as the latter is small for protons[4] and large for fluorine.[2] It is shown more directly by the recent molecular beam measurements of the spin-rotation interaction constant for the proton and fluorine nuclei in HF, which give $|c_p| = 71$ kc/sec and $|c_\mathrm{F}| = 305$ kc/sec.[5] The contribution to $1/T_1$ goes as the square of the interaction constant,[1] so the relaxation of protons should be only 1/10 to 1/100 as effective as for fluorine.[6]

Secondly, although the temperature dependence of spin relaxation via the spin-rotation interaction is difficult to calculate in detail, the observed limits are compatible with theory. The interaction, in general, is of the form $\vec{\mu}\cdot c\cdot\vec{J}$, where $\vec{\mu}$ is the nuclear magnetic moment, c is the spin-rotation interaction dyadic, and $\vec{J}$ the molecular angular momentum. Spin-lattice relaxation occurs because molecular collisions cause m_J and also J to change, thereby producing fluctuations in the rotational magnetic field at the nuclei. If, for simplicity, we consider a linear molecule and assume that all the relaxation processes are governed by the same correlation time, the fluorine T_1 for $\omega^2\tau_c^2 \ll 1$ is given by an expression of the form,[1,7]

$$1/T_{1\mathrm{F}} = \tau_c[A + Cc_\mathrm{F}^2\langle J(J+1)\rangle]. \qquad (2)$$

The first term includes the nuclear dipole-dipole and $\Delta\sigma$ contributions and the second, the spin-rotation effects. However, $\langle J(J+1)\rangle$ is proportional to the rotational energy which approaches RT at high temperatures and zero at low.

This agrees with the high- and low-temperature limits in R_{obs}, except that Eq. (2) predicts the same $T=0$ intercept for the high- and low-temperature straight-line portions of the curves in Fig. 2. The origin of the discrepancy may be seen by comparing the relative magnitudes in Eq. (2) of the mean square dipolar field A, at a fluorine nucleus, and the mean square rotational field, $Cc_\mathrm{F}\langle J(J+1)\rangle$. The latter should be of the order of 10 to 100 times the former, even at 100°K, and R should also be 10 to 100 instead of ≈ 1 as observed. Therefore, it appears that the spin-rotation contribution to $1/T_1$ is "quenched" by intermolecular interactions at lower temperatures and that the quenching becomes less important at higher temperatures, which seems reasonable. In other words, the assumption in Eq. (2) that the nuclear relaxation is governed by a single correlation time for all processes is much too drastic. Allowance must be made for relaxation among rotational states and, in fact, an interesting feature of these results is the possibility of studying such processes by means of nuclear T_1 and T_2 observations. Work along these lines is in progress.

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[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[2] H. S. Gutowsky and D. E. Woessner, Phys. Rev. 104, 843 (1956).

[3] This sample, as well as some of the others, exhibits hysteresis and anomalies in the T_1's measured, probably as a result of residual traces of O_2 adsorbed on the glass sample tubes. It is hoped that more reliable data can be obtained in experiments now under way with "getter" techniques to eliminate O_2. See H. S. Sandhu, J. Lees, and M. Bloom, Can. J. Chem. 38, 493 (1960).

[4] N. F. Ramsey, Nuclear Moments (John Wiley & Sons, Inc., New York, 1953), p. 73.

[5] M. R. Baker and N. F. Ramsey, Bull. Am. Phys. Soc. 5, 344 (1960). See also M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. 121, 807 (1961), p. 815, on which the implications for nuclear relaxation of the large c_F are discussed.

[6] A study was made of the proton and fluorine T_1 and T_2 in liquid HF at room temperature by I. Solomon and N. Bloembergen, J. Chem. Phys. 25, 261 (1956), and the results were interpreted without recourse to spin-rotation interaction. This is reasonable for pure HF, because in it the strong hydrogen bonding and resultant polymerization could quench the interaction. [See also the footnote in the paper on T_1 in liquid H_2: W. P. A. Hass, G. Seidel, and N. J. Poulis, Physica 26, 834 (1960)]. However, in aqueous solutions of HF they found the fluorine T_1 to be much shorter than the proton T_1 and attributed the differences to differential molecular association and chemical exchange effects. Another possibilty is that the water decreases the quenching of the spin-rotation interaction in the HF. The importance of the latter probably could be assayed by observing the temperature dependence of T_1 and T_2.

[7] The details can be developed in a manner similar to that described by I. Solomon, Phys. Rev. 99, 559 (1955); see also Solomon and Bloembergen, reference 6.

GENERAL ANALYSIS OF OPTICAL, INFRARED, AND MICROWAVE MASER OSCILLATOR EMISSION*

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In this paper we will generalize the equations governing coherent emission from quantum mechanical amplifiers (microwave, infrared, and optical masers) using either electric or magnetic dipole transitions. Earlier analyses by Gordon, Zeiger, and Townes,[1] Feynman, Vernon, and Hellworth,[2] and Wang and Singer,[3] are incorporated in our generalization. The principal new result of our analysis is that we find that an amplitude modulation of the output is to be expected from all maser oscillators excepting those in which excited atoms are supplied at a notably greater rate than the depopulation rate due to coherent induced emission. This analysis also suggests that energy population inversions of electric dipole moments can be performed using coherent light sources in the same manner as with magnetic dipole moments. It appears, therefore, that modulation of an optical or infrared maser (e.g., for communication purposes) may be easily accomplished by varying the population of excited states through control of the pumping energy. This modulation may be both by absorption and by amplification. Amplitude modulation of maser oscillators has been observed in this laboratory[3] and elsewhere[4-6] and we will explain these observations.

The total density of active atoms is composed of n_2, the density of upper energy state molecules, times the relative quantum (statistical) weights g_1/g_2, and n_1, the density of lower energy state atoms. We define the difference as the effective number of molecules given by

$$N_e \equiv n_2(g_1/g_2)-n_1. \tag{1}$$

N_e is dependent on the pumping system. For nondegenerate levels, $g_1/g_2=1$. The superposition state of a molecule may be described by

$$\psi = a_1(t)u_1 + a_2(t)u_2, \tag{2}$$

where $|a_1(t)|^2$ is the time-dependent probability coefficient of the lower state and $|a_2(t)|^2$ is the time-dependent coefficient for the upper state. The two states are orthogonal and may be normalized, but the existence of other states must be considered in such a normalization procedure. The frequency of transition is given by

$$\omega_0 = (W_2 - W_1)\hbar, \tag{3}$$