state is

$$\sigma^2 = \langle (n-n_0)^2 \rangle = \sum |A_n^{(0)}|^2 (n-n_0)^2 / \sum |A_n^{(0)}|^2,$$

or, using Eq. (5.3),

$$\sigma^2 = \frac{n_0}{1 + 2(\alpha^2)^{1/2} n_0 / q_0}. \qquad (5.4)$$

The bottom row of Table I shows σ^2 for four limiting cases. The dispersion [Eq. (5.4)] is in every case smaller than the classical dispersion obtained from a Poisson distribution, namely $\sigma^2 = n_0$,[6] although for $r \gtrsim c$ the dispersion is of order n_0, the average photon number. When the amount of energy in the electromagnetic field greatly exceeds the amount of energy available to

the uncoupled atoms, $c \gg r$, then the dispersion is much less than the average photon number, $n_0 \cong c$, and is $\sim r$ instead.

Note added in proof. Figure 3 should have $2q$ everywhere instead of q, as in Fig. 4. Also, Fig. 5 defines $-F(n)$, not $F(n)$.

ACKNOWLEDGMENTS

Nonexponential Spin-Lattice Relaxation of Protons in Solid CH₃CN and Solid Solutions of CH₃CN in CD₃CN*

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The proton spin-lattice relaxation in solid CH₃CN, and in 1:6 and 1:10 solid solutions of CH₃CN in CD₃CN, has been measured by pulsed NMR techniques at a frequency of 30.0 MHz, for temperatures between 79.5 and 173°K. The relaxation is nonexponential at the higher temperatures, and exponential only at the lowest temperature. The experimental results for 1:6 solutions are compared with the relaxation previously predicted by a calculation based on the assumptions that (1) the relaxation is due to intramolecular dipole-dipole interactions between protons, which are time-dependent because of hindered rotations of the methyl groups, (2) the axes of hindered rotation are randomly oriented, and (3) the correlation time for reorientation is the same for all methyl groups at the same temperature. The distinctly nonexponential relaxation predicted by the theory is due to the inclusion of the effects of the cross correlations of the intramolecular dipole-dipole interactions. The agreement between the experimental results and the calculations is fairly good, the discrepancy being attributable to the effects of other relaxation mechanisms, such as intermolecular dipole-dipole interactions. The results provide the first experimental evidence of nonexponential spin-lattice relaxation produced by the effects of cross correlations of dipole-dipole interactions.

I. INTRODUCTION

THE nuclear magnetic relaxation of spin-$\frac{1}{2}$ nuclei is due in many cases mainly to nuclear magnetic dipole-dipole interactions, which are time-dependent as a result of the motion of the nuclei. The calculation of the nuclear magnetic relaxation involves certain correlation functions of each dipole-dipole interaction with itself (autocorrelations) and with other dipole-dipole interactions (cross correlations). If the cross-correlation terms are omitted, the calculated relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays.[1] If the cross-correlation terms are included in the calculation,

the longitudinal relaxation is found, in general, to be the sum of more than one decaying exponential.

Calculations of the relaxation of systems of three and four identical spin-$\frac{1}{2}$ nuclei in molecules undergoing isotropic rotational Brownian motion have shown that there is little difference in the relaxation predicted when cross correlations are included and the exponential relaxation predicted when cross correlations are omitted.[2-6]

One situation for which the inclusion of cross correlations in the calculation has led to the prediction of a distinctly nonexponential spin-lattice relaxation is the case of three identical spin-$\frac{1}{2}$ nuclei at the corners of an equilateral triangle which undergoes hindered rotations

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[1] P. S. Hubbard, Rev. Mod. Phys. **33**, 249 (1961).

[2] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958); **111**, 1746 (1958).
[3] P. S. Hubbard, Phys. Rev. **128**, 650 (1962).
[4] G. W. Kattawar and M. Eisner, Phys. Rev. **126**, 1054 (1962).
[5] P. M. Richards, Phys. Rev. **132**, 27 (1963).
[6] L. K. Runnels, Phys. Rev. **134**, A28 (1964).

about an axis perpendicular to the plane of the three spins and oriented at a fixed angle β, with respect to the constant magnetic field $H_0\mathbf{k}$.[6,7] Two models for the rotation about the axis have been considered: (1) random jumps of 120° between equilibrium positions, with a probability per unit time, ν, of a jump to a new orientation, and (2) rotational diffusion about the axis. Both models lead to results of the same form, which differ only in the definition of the correlation time τ_c of the reorientation. For model (1), $\tau_c = (2/3\nu)$, and the relaxation is independent of the orientation of the equilibrium positions about the axis. For model (2), τ_c is related to the rotational-diffusion coefficient. Also, the average relaxation has been calculated for situations in which the axes of rotation are isotropically oriented and each 3-spin system has the same correlation time for reorientation about its symmetry axis. The calculations have shown that the average of the exponential relaxation obtained for each angle, when cross correlations are neglected, is approximately a simple exponential decay, and is much less nonexponential than the average obtained when cross correlations are included.[7]

The nuclear magnetic relaxation of the protons in methyl groups in solids has been extensively investigated.[8] The relaxation at some temperatures has been interpreted as being due to intramolecular dipole-dipole interactions modulated by hindered rotations. However, no observations of a nonexponential spin-lattice relaxation have been reported, as far as we know. Values of a spin-lattice relaxation time T_1 have been quoted, implying a simple exponential decay, and the experimental values have been compared with values calculated from theories in which cross correlations are omitted.[8]

One of the simplest systems studied previously[8] is solid acetonitrile, CH_3CN. Proton line-shape studies indicate that the only significant motions of the CH_3 groups in the temperature range from 100°K to the melting point are reorientations about their symmetry axes.[9] The effect of a nitrogen magnetic moment on the relaxation of the protons in the same molecule can be shown to be negligible as a result of the facts that the magnetic moment of a nitrogen nucleus is smaller than that of a proton, and a nitrogen nucleus is farther from a proton in a CH_3CN molecule than the other two protons. The effect of dipole-dipole interactions between spins in different molecules is not negligible, but can be reduced by diluting CH_3CN in CD_3CN.

We report here measurements of the spin-lattice relaxation of the protons in solid CH_3CN, and in solid solutions of one part CH_3CN to six parts CD_3CN and one part CH_3CN to ten parts CD_3CN, at temperatures between 79.5 and 173°K. The relaxation has been found to be nonexponential in all the solid samples at all but the lowest temperature. The experimental procedure is described in Sec. II. In Sec. III the experimental results are presented and are compared with the nonexponential relaxation predicted by the calculations in which cross correlations are included.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Samples

Three sets of samples were made, each consisting of three samples with different ratios of CH_3CN to CD_3CN: one sample of pure CH_3CN, and two samples with 1:6 and 1:10 ratios of CH_3CN to CD_3CN, respectively. The ratios refer to volumes of the liquid constituents at room temperature, and are estimated to be accurate to within 5%.

The CD_3CN used in the samples was obtained from Nuclear Magnetic Resonance Specialties, Inc., and has a quoted isotopic purity of 99%. The Spectro Grade CH_3CN used in the first two sets of samples was obtained from the Eastman Kodak Co. The CH_3CN used in the third set of samples was obtained from John Holz, who purified it by permanganate distillation followed by fractional distillation, and verified by ultraviolet absorption that it was at least 99% pure.

The sample containers consisted of a $\frac{5}{8}$-in.-long bulb of 11-mm o.d. standard wall Pyrex tubing attached to a 4-in. length of 2-mm i.d. capillary tubing, which was attached to a 23-in. length of 9-mm o.d. Pyrex tubing used to position samples in the coils within a Dewar. The samples were prepared by filling the bulb with $\frac{1}{2}$ in. of the liquid sample, removing dissolved oxygen by the freeze-pump-thaw technique, and sealing the sample at a point in the capillary tubing.

Corresponding samples of the three sets had the same spin-lattice relaxation in the solid state, within experimental uncertainty. The results presented below were obtained with the third set of samples.

B. Temperature-Control Apparatus

Temperatures between 91 and 173°K were produced by cold nitrogen gas flowing through the probe, which was in a Dewar. The cold nitrogen gas was produced by boiling liquid nitrogen with a heater immersed in a 50-liter Dewar. The temperature of the sample was monitored by a copper-constantan thermocouple placed $\frac{1}{4}$ in. below the sample, which activated a Leeds & Northrup Type-60 control unit connected to the heater. The temperature was recorded on a calibrated Leeds & Northrup recorder. The temperature varied less than 0.3°K during the measurement of any relaxation curve. The system was calibrated, and additional thermocouples employed to show that the quoted temperatures represent the temperatures of the sample to within ±0.8°K, and that the temperature variations over the samples were less than 0.4°K.

[7] R. L. Hilt and P. S. Hubbard, Phys. Rev. **134**, A392 (1964).
[8] For example, see E. O. Stejskal, D. E. Woessner, T. C. Farrar, and H. S. Gutowsky, J. Chem. Phys. **31**, 55 (1959).
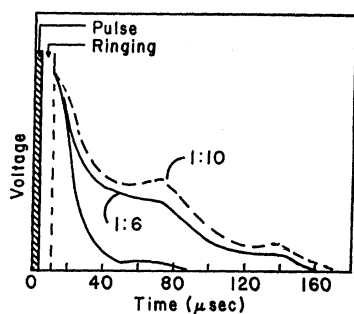[9] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950).

FIG. 1. Proton free-induction decay signal observed after 90° pulse applied to solid sample of CH_3CN and 1:6 and 1:10 solid solutions of CH_3CN in CD_3CN. The curves are normalized so that the signal voltages are equal at the end of the receiver recovery time.

A stable temperature of 79.5°K was obtained by filling the Dewar containing the probe with liquid nitrogen.

C. Pulsed NMR Apparatus

A conventional pulsed NMR apparatus with a crossed-coil probe was employed, operated at 30.0 MHz. The constant magnetic field of 7.05 kG was produced by a 12-in. Harvey-Wells electromagnet with a 3-in. gap. The receiver coil was coupled to a 2-MHz bandwidth LEL Model IMM-2 receiver having a diode detector.

The output-versus-input response of the receiver-detector system was measured, and was found to be linear for output voltages between 0.4 and 4.2V. The gain of the receiver was adjusted so that the measured voltages in each experiment were within the linear range. The results were corrected to take account of the fact that the linear part of the response curve did not extrapolate through the origin.

The recovery time of the receiver system after a rf pulse was 7–8 μsec.

Most of the measurements were made with a rf field which produced a 90° pulse for protons of duration 3–3.5 μsec. A few measurements were made with an rf field corresponding to a 90° pulse of 4.2 μsec. The longer pulse length did not affect the measured relaxation, to within experimental error.

The initial tuning of the apparatus was performed by maximizing the spin echo following a 90°-t-180° pulse sequence applied to a low-melting-point liquid sample. The final tuning consisted of adjusting the magnetic field and the duration of a 180° pulse so that there was no nuclear signal following a 180° pulse applied to a solid sample of CH_3CN.

D. Relaxation Measurements

The spin-lattice relaxation following a 180° pulse is represented by the time dependence of the quantity $R(t) = \frac{1}{2}\{1 - [M_z(t)/M_0]\}$, where $M_z(t)$ is the longitudinal component of the nuclear magnetization at a

time t after a 180° pulse is applied to the system in thermal equilibrium, and M_0 is the thermal equilibrium nuclear magnetization. The quantity $M_z(t)/M_0$ has been determined by dividing the signal amplitude following a 90° pulse applied at a time t after a 180° pulse was applied to the system in thermal equilibrium, by the corresponding signal amplitude following a 90° pulse applied to the system in thermal equilibrium.

The shape of the free-induction decay signals following a 90° pulse applied to solid samples of CH_3CN, 1:6 CH_3CN in CD_3CN, and 1:10 CH_3CN in CD_3CN at 113°K are shown in Fig. 1. The amplitudes have been normalized to the same magnitude at the end of the receiver overload. The decreasing decay rate with increasing dilution presumably results from a decrease in the effect of intermolecular dipole-dipole interactions between protons.

In the determination of M_0 and $M_z(t)$ for a particular sample at a given temperature, the nuclear signal following a 90° pulse was taken to be the amplitude of the free-induction decay signal at a fixed time after the end of the rf pulse. The choice of the time, within the range 8–10 μsec, did not affect the results for $R(t)$.

The signal amplitudes were measured by use of a Tektronix Type-RM31A oscilloscope with a Type-Z calibrated differential comparator plug-in unit.

III. RESULTS

The longitudinal relaxation following a 180° pulse, $R(t) = [M_0 - M_z(t)]/2M_0$, has been measured for protons in solid samples of CH_3CN, and in solid solutions of CH_3CN in CD_3CN in the ratios of 1:6 and 1:10. The results at the temperature 123°K for the three different compositions are plotted on a logarithmic scale in Fig. 2. The faster relaxation of the pure sample compared to the 1:6 sample, and of the 1:6 sample compared to the 1:10 sample, is presumably due to intermolecular dipole-dipole interactions between protons. It would appear that intermolecular interactions are probably not completely negligible even for the 1:10
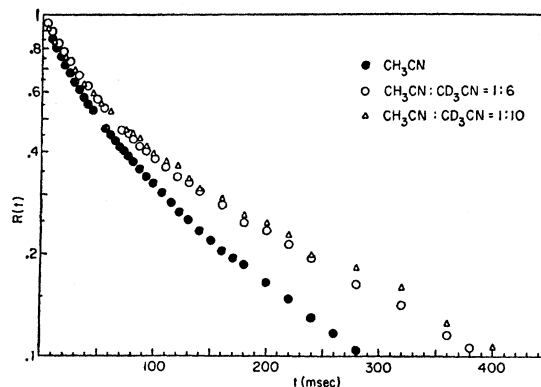

FIG. 2. Proton spin-lattice relaxation in CH_3CN and in 1:6 and 1:10 solutions of CH_3CN in CD_3CN at 123°K. $R(t) \equiv [M_0 - M_z(t)]/2M_0$.

FIG. 3. Spin-lattice relaxation $R(t) \equiv [M_0 - M_z(t)]/2M_0$ of 3-spin systems following 180° pulse. The solid curves are calculated results for different values of $\omega_0 \tau_c \leq 0.701$. The dashed curves are experimental results for the proton relaxation at different temperatures in 1:6 solid solutions of CH_3CN in CD_3CN. $1/T' \equiv (\gamma^4 \hbar^2 / r_0^6 \omega_0) = 76.8$ sec^{-1}.
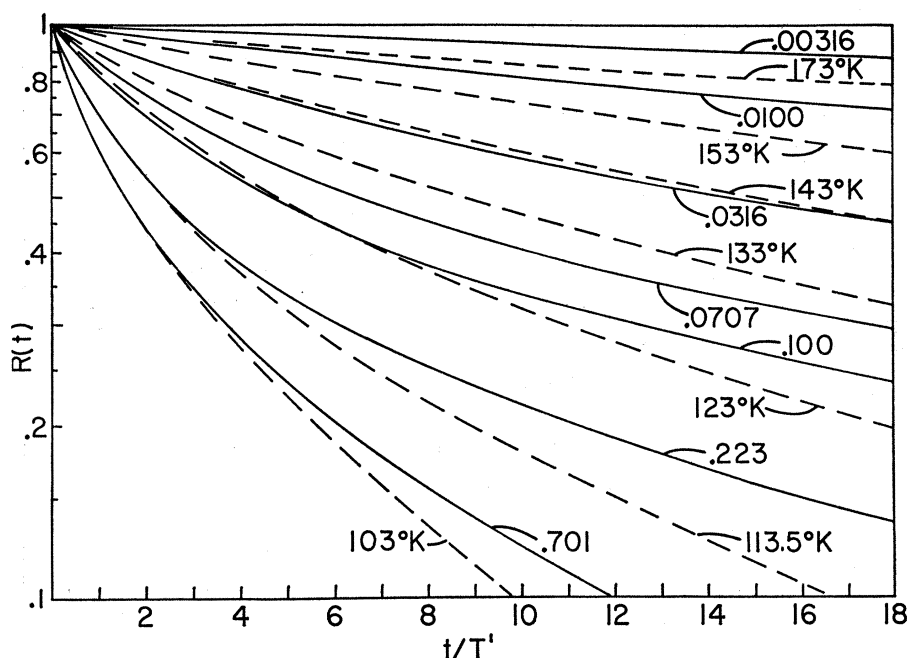
sample. It can be observed from Fig. 2 that the relaxation is distinctly nonexponential, even in the case of pure CH_3CN, where intermolecular dipole-dipole interactions are certainly significant.

In the determination of the relaxation curves, more data points were taken than could be shown in Fig. 2. Also, each point on a curve is the average of the results obtained from several repetitions of the pulse sequence used to determine $M_z(t)$ and M_0. The times between the pulse sequences were always at least 20 times the effective relaxation time of the spin system, so that the spin system was in thermal equilibrium at the beginning of each pulse sequence. The scatter of the points in Fig. 2 is typical of all our experimental results. Individual data points will not be displayed henceforth. The uncertainty of our experimental results is somewhat greater than is indicated by the scatter of the points in Fig. 2. Repetitions of the determination of $R(t)$ at nominally the same temperatures for the same sample on different days, and for different samples of nominally the same composition and temperature, resulted in relaxation curves which sometimes differed by as much as 5%, although the nonexponential *shapes* of the curves did not differ appreciably. It should be noted that, in spite of this uncertainty, the relaxation of the 1:10 samples was consistently slower than the relaxation of the 1:6 samples.

The results presented hereafter are all for 1:6 solid solutions of CH_3CN in CD_3CN. Most of our measurements were made on samples of this composition, since the signal-to-noise ratio for 1:10 samples was poor, and there are clearly significant intermolecular interactions in the pure samples.

We assume that our samples were polycrystalline, and

that the axes of rotation of the methyl groups were oriented isotropically. Evidence for this assumption is provided by the facts that the relaxation was unchanged by rotation of the samples about an axis perpendicular to the magnetic field, and essentially the same results were obtained for different samples at the same temperature. Since the structure of the small crystals constituting the polycrystalline samples is not known, it is not certain that all methyl groups had the same environment, and hence the same correlation time for reorientation at a given temperature. Nevertheless, for lack of a better model, we shall compare our data with results calculated on the assumptions that the relaxation is due to intramolecular dipole-dipole interaction between protons, the axes of rotation are randomly oriented, and the correlation times of all methyl groups are equal at a given temperature.

The theoretical values of the relaxation $R(t)$, calculated as previously described,[7] are plotted logarithmically versus t/T' in Fig. 3 for selected values of $\omega_0 \tau_c \leq 0.701$, and in Fig. 4 for selected values of $\omega_0 \tau_c \geq 1.00$. By definition, $1/T' \equiv (\gamma^4 \hbar^2 / r_0^6 \omega_0)$, where γ is the gyromagnetic ratio of the spin-$\frac{1}{2}$ particles, ω_0 is the Larmor frequency in radians per second, and r_0 is the distance between the spins in the 3-spin system.

The experimental results for $R(t)$ for the 1:6 solutions at different temperatures are also plotted in Figs. 3 and 4 as dashed curves. The value of T' used was determined as follows. Let the "null point" t_0 be defined by $R(t_0) = \frac{1}{2}$. From the theoretical curves for $R(t)$ versus t/T' shown in Figs. 3 and 4, and from theoretical curves for other values of $\omega_0 \tau_c$ not shown, one can determine t_0/T' for the different values of $\omega_0 \tau_c$. A graph of $\ln(t_0/T')$ versus $\ln(\omega_0 \tau_c)$ is shown in Fig. 5. The mini-
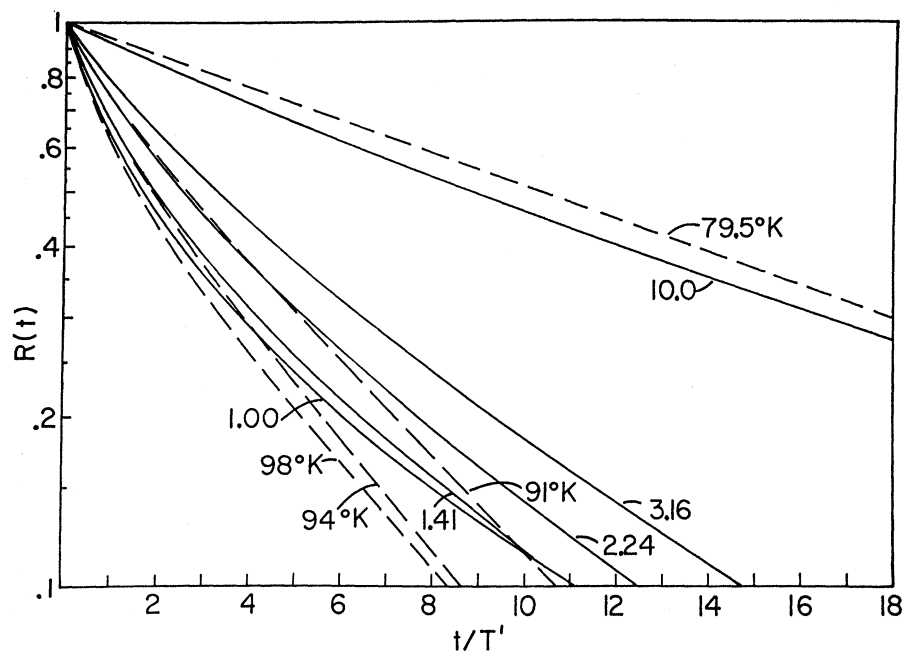
Fig. 4. Spin-lattice relaxation $R(t) \equiv [M_0 - M_z(t)]/2M_0$ of 3-spin systems following 180° pulse. The solid curves are calculated results for different values of $\omega_0 \tau_c \geq 1.00$. The dashed curves are experimental results for the proton relaxation at different temperatures in 1:6 solid solutions of CH_3CN in CD_3CN.

mum value of t_0/T' is 1.52, at $\omega_0 \tau_c = 0.68$. On the other hand, from the experimental results for $R(t)$ one can obtain the plot of $\ln t_0$ versus $1/T$ shown in Fig. 6, which has a minimum at $t_0 = 19.8$ msec. In order for the minimum t_0 determined theoretically to agree with the minimum t_0 determined experimentally, one must therefore take $1/T' = 76.8$ sec^{-1}. Since for protons $\gamma = (2.675)10^4$ sec^{-1}G^{-1}, and for our experiments $\omega_0 = (1.885)10^8$ sec^{-1}, it follows from $1/T' = 76.8 = (\gamma^4 \hbar^2/r_0^6 \omega_0)$ that $r_0 = (1.844)10^{-8}$ cm. This value is in reasonably good agreement with the value $(1.814)10^{-8}$ cm for the proton-proton distance in gaseous CH_3CN, which can be calculated from previously reported dimensions of the molecule.[10] Although the value of r_0 for CH_3CN in a solid might differ from the value in a gas, it is probable that our value is not very accurate.

Since the minimum value of t_0 determined from the experimental results plotted in Fig. 6 is estimated to be accurate to within 3%, one might expect that our deter-

mination of r_0 would have an uncertainty of less than $\frac{1}{2}$%. However, it must be remembered that our determination is based on the assumption that the relaxation in the 1:6 solutions is due just to intramolecular dipole-dipole interactions, which is not entirely correct, since Figs. 1 and 2 indicate that intermolecular interactions are not completely negligible.

It may be noted parenthetically that, if the relaxation were a simple exponential decay with time constant T_1, the relaxation time T_1 would be given in terms of the null time t_0 by $T_1 = t_0/\ln2 = 1.443 t_0$. The scale on the right-hand side of Fig. 6 is for such effective values of T_1.

It is plausible to suppose that the correlation time τ_c decreases with increasing temperatures. This assumption is sufficient in most cases to determine on which of the Figs. 3 or 4 the experimental results for the relaxa-
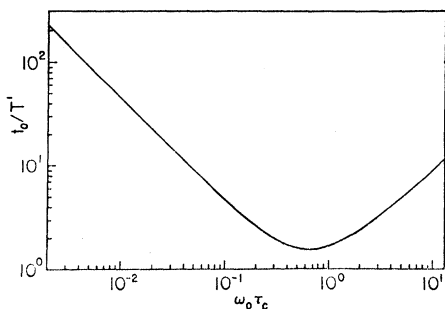

Fig. 5. Dependence of t_0/T' on $\omega_0 \tau_c$, as predicted by the theory.

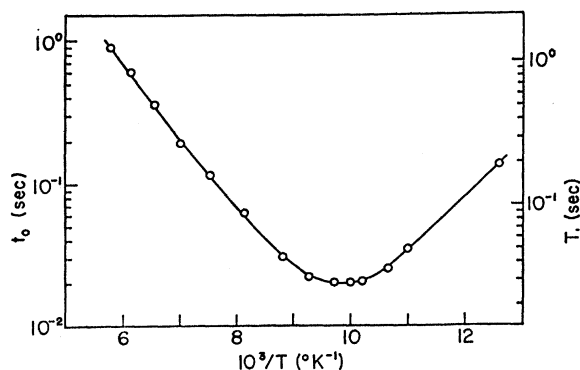[10] L. F. Thomas, E. I. Sherrard, and J. Sheridan, Trans. Faraday Soc. **51**, 619 (1955).

Fig. 6. Dependence of the experimentally determined null point t_0 on the temperature, for 1:6 solid solutions of CH_3CN in CD_3CN. The scale on the right-hand side is for the effective relaxation time $T_1 \equiv t_0/\ln 2$.

tion at different temperatures should be plotted. Ambiguities occur only for temperatures corresponding to $\omega_0\tau_c \cong 1$, and these are resolved in a manner explained below.

The values of $\omega_0\tau_c$ to be associated with the experimental results at different temperatures are not in general equal to the discrete values of $\omega_0\tau_c$ for which calculated results for $R(t)$ are available. However, one can interpolate by using Fig. 5, from which one can obtain the values of $\omega_0\tau_c$ corresponding to the value of t_0/T' calculated from the experimental results at the different temperatures. This procedure corresponds to matching an experimental relaxation curve to the theoretical relaxation curve that would have the same null point t_0. The values of $\omega_0\tau_c$ determined in this manner are plotted as open circles in Fig. 7 as a function of $1/T$. This procedure is not satisfactory for the three temperatures 98, 100, and 103°K, for which the experimental values of t_0/T_1 are approximately equal, and fall on the broad minimum of Fig. 5. Hence, the values of $\omega_0\tau_c$ for these temperatures were determined from the smooth curve drawn through the open circles in Fig. 7, and are shown as black circles in that figure. The values of t_0/T' from Fig. 5 corresponding to the three values of $\omega_0\tau_c$ determined in this manner are approximately equal, which is consistent with the experimental results. This procedure provides a method of determining on which of Figs. 3 or 4 the ambiguous cases, for which $\omega_0\tau_c \cong 1$, should be plotted.

One of the results of the calculations described in Ref. 7 is that the relaxation $R(t)$ considered as a function of t/T_0, where $1/T_0 \equiv \gamma^4\hbar^2\tau_c/r_0{}^6 = \omega_0\tau_c/T'$, is the same function for all τ_c for which $(\omega_0\tau_c)^2 \ll 1$. This is true for each orientation of the axis of rotation, with different functions depending on the angle, and hence it is also true for the relaxation averaged over orientation. The calculated function R of t/T_0 for the case of
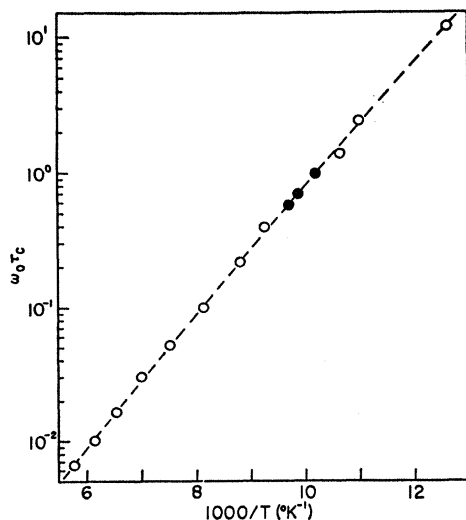

FIG. 7. Values of $\omega_0\tau_c$ of methyl groups in 1:6 solid solutions of CH_3CN in CD_3CN at different temperatures. $\omega_0 = (1.885)10^8$ sec^{-1}.
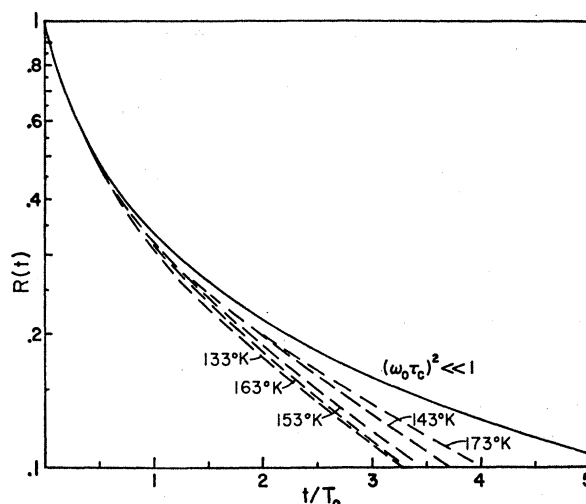

FIG. 8. Spin-lattice relaxation $R(t) \equiv [M_0 - M_z(t)]/2M_0$ of 3-spin systems following 180° pulse, for $(\omega_0\tau_c)^2 \ll 1$. The solid curve is the theoretical prediction. The dashed curves are experimental results for different temperatures corresponding to $(\omega_0\tau_c)^2 \ll 1$. $1/T_0 \equiv \gamma^4\hbar^2\tau_c/r_0{}^6 = \omega_0\tau_c/T'$.

isotropic orientation and $(\omega_0\tau_c)^2 \ll 1$ is shown in Fig. 8 as a solid line. Since the value of τ_c corresponding to the experimental data at each temperature has been evaluated by the procedure described above, it is possible to calculate the value of T_0 for each temperature, and to plot the experimental relaxation versus t/T_0. The results for the temperatures for which $(\omega_0\tau_c)^2 \ll 1$ are plotted in Fig. 8 as dashed lines. As in Figs. 3 and 4, the experimental results agree well with the theory for small values of t, and fall off more rapidly for larger values of t. The differences between the experimental curves in Fig. 8 at the larger values of t/T_0 may not be significant since the differences may well be due to experimental errors, which have more effect on the determination of $R(t)$ for small values of $R(t)$ than for large values.

Figure 8 displays better than Figs. 3 and 4 that the experimental relaxation for the higher temperatures in the solid is quite nonexponential.

We have also measured the spin-lattice relaxation of protons in liquid samples of CH_3CN, and 1:6 solutions of CH_3CN in CD_3CN, at $-30°C$, and in liquid samples of glycerol at room temperature. The fact that a simple exponential relaxation was measured in all the liquid samples, and in the solid samples at the lowest temperature, indicates that the nonexponential relaxation measured at other temperatures in the solid samples was not the result of errors in the experimental procedures.

IV. DISCUSSION

The results contained in Figs. 3, 4, and 8 can be described as follows: If the correlation time τ_c corresponding to each temperature is chosen so that the experimental and theoretical relaxations agree at time t_0, then the time dependence of the experimental relaxation agrees with the theory for $t \lesssim t_0$, and is more rapid than

the theory for $t > t_0$. This behavior can be explained by the fact that there are other relaxation mechanisms present in addition to the intramolecular dipole-dipole interactions between spins, for which the theoretical curves were calculated.

From the theoretical curves it is apparent that $(d/dt)[\ln R(t)]$ is negative and decreases in magnitude as t increases from zero. If there were another relaxation mechanism which by itself would produce an exponential relaxation with time constant T_1', this mechanism could be expected to contribute a term $-1/T_1'$ to the total $(d/dt)[\ln R(t)]$. The term $-1/T'$ would have more effect for large values of t, since the magnitude of the theoretical $(d/dt)[\ln R(t)]$ decreases with increasing t. Hence, while the experimental rate of relaxation would be faster than predicted by the theory for all values of $t > 0$, the difference should increase with increasing time. This is what is observed.

An additional relaxation mechanism which is present in the 1:6 deuterated solutions consists of intermolecular dipole-dipole interactions between protons, as is demonstrated by Fig. 2, which shows that a 1:6 solution relaxes more rapidly than a 1:10 solution. The relaxation effect of a nitrogen nucleus on the protons in the same molecule is smaller than the effect of intramolecular dipole-dipole interactions between protons by approximately the factor $\frac{1}{2}(\mu_N/\mu_H)^2(r_{HH}/r_{HN})^6 \simeq 0.003$, and hence is negligible. Intermolecular dipole-dipole interactions of protons with nitrogen nuclei, and with deuterons in the deuterated samples, are almost certainly smaller than the proton intermolecular effects in the pure CH_3CN, but are not necessarily smaller than the proton intermolecular effects in the deuterated samples. The relaxation effects of spin-rotational interactions of the protons, and of interactions with paramagnetic impurities such as oxygen, cannot be excluded entirely but are probably negligible.

The theoretical results with which the data have been compared were calculated on the assumptions that the relaxation is due to intramolecular dipole-dipole interactions between protons, the axes of hindered rotation are isotropically oriented, and the correlation times for all methyl groups are the same at a given temperature. The effects of the cross correlations of the intramolecu-

lar dipole-dipole interactions were included. It is interesting to note that the observed nonexponential relaxation cannot be explained by a calculation based on the same assumptions given above, but in which cross correlations of the intramolecular dipole-dipole interactions are omitted. For such a model, the relaxation of a methyl group whose axis of rotation is at an angle β with respect to the applied magnetic field is a simple exponential decay with relaxation time T_1, which is a function of β.[7] Nevertheless, the average relaxation of a sample in which the axes of orientation are isotropically oriented is in principle nonexponential, since the average of an exponential with a varying time constant is not a simple exponential. However, calculations have shown that the average relaxation when cross correlations are omitted differs so little from a simple exponential decay that there is poor agreement with the distinctly nonexponential experimental results presented here.[11]

Perhaps the strongest evidence that the experimentally observed nonexponential relaxation is due to the effect of cross correlations of intramolecular dipole-dipole interactions is the temperature dependence of the curvature of $\ln R(t)$. According to the theory, the relaxation is distinctly nonexponential for $\omega_0\tau_c \lesssim 1$ (see Figs. 3 and 8), but is approximately exponential for $(\omega_0\tau_c)^2 \gg 1$. The latter fact is not obvious from Fig. 4, but is apparent if the theoretical results for values of $(\omega_0\tau_c)^2 \gg 1$ are plotted on a scale which displays more of the decay. These theoretical predictions are in agreement with the experimental results that the relaxation in the solid is exponential at low temperatures but nonexponential at higher temperatures.

V. CONCLUSIONS

The spin-lattice relaxation of the protons in solid CH_3CN and in solid solutions of CH_3CN in CD_3CN is nonexponential over a wide range of temperature. The nonexponential relaxation can be attributed to the effects of cross correlations of intramolecular dipole-dipole interactions. The results reported here are the first example of such an effect.

[11] A few of the results of such calculations are shown in Fig. 5 of Ref. 7.