# THE DESCRIPTION AND USE OF A SPIN-ECHO SPECTROMETER TO STUDY CHEMICAL EXCHANGE<sup>1</sup>

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#### ABSTRACT

A spin-echo spectrometer, suitable for studies of chemical exchange, is described. The performance of the apparatus is described and illustrated. From a Carr-Purcell sequence of pulses  $T_2$  measurements have been made using two alternative schemes for the correction of cumulative error in the width of  $\pi$  pulses. Agreement is satisfactory and the standard errors in each method are  $\pm 5\%$  of the average  $T_2$ . The Meiboom and Gill method of phase-shifting the r.f. in the first pulse has the advantage of more flexibility in the choice of pulse intervals.

A theory developed by Bloom, Reeves, and Wells for the dependence of  $T_2$  measured in a Carr-Purcell experiment on pulse intervals in the presence of a suitable exchange process has been tested experimentally for two molecules. The rate constants for the hindered internal rotation about the N==N bond in N,N-dimethylnitrosamine agree for the following sets of data: (a) a previous high-resolution study by Phillips, (b) a repeated high-resolution study made in this work, (c) spin-echo studies using the complete closed expression for a two site exchange process, and (d) the approximate expression derived for the limit of fast pulse repetition rates.

A similar study by the spin-echo method of the rates of internal rotation about the C==N bond in N, N-dimethyltrifluoroacetamide does not agree with a previous high-resolution study. Since the chemical shift between the inequivalent methyl groups is so small, it is suggested that the rates of rotation in this molecule are much better evaluated by the spin-echo method.

The spin-echo method can more easily take account of variations with temperature of the natural relaxation time and the chemical shift. The non-selective nature of an experiment with such a large  $H_1$  field remains a disadvantage at this time. The selective deuteration of sites unaffected by exchange is in general difficult enough to limit the scope of the spin-echo method when protons are observed. when protons are observed.

# INTRODUCTION

The time constant for the decay of echo amplitudes in a Carr-Purcell spin-echo experiment (2) is affected by the pulse interval, even in a homogeneous magnetic field, if there is a chemical exchange which modulates the Larmor frequencies at a rate comparable to the frequency difference (17, 3, 4). The general solution for the decay of echo amplitudes has been presented by Bloom, Reeves, and Wells (1) for the case of exchange involving two Larmor frequencies in the absence of spin-coupling. From considerations of simple probability theory for phase angle distribution in the x'y' plane and the use of a matrix operator technique to generate the amplitude of alternate echoes, it can be shown that the magnetization at a time  $4n\tau$  is related to the initial magnetization by an expression involving the sum of two exponentials;

$$M(4n\tau) = A_1 \exp(-r_1 4n\tau) + A_2 \exp(-r_2 4n\tau)$$

[1]  $M(4n\tau) = A_1 \exp(-r_1 4n\tau) + A_2 \exp(-r_2 4n\tau)$ where  $\tau = \frac{\pi}{2}$ ,  $\pi$  pulse interval, n = 0, 1, 2... etc.,  $A_1$  and  $A_2$  are constants which depend upon the initial conditions, and  $r_1$  and  $r_2$  are two time constants, which are independent of the initial conditions. A similar relationship has been derived (5) by the use of the Bloch equations (6).

In this paper, experimental results will be presented for two special cases when the

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population of one site is equal to that of the other. In this event a single time constant  $r_1$  dominates the decay of echo amplitudes and this is given by (1)

[2] 
$$r_1 = k - \frac{1}{2\tau} \sinh^{-1} F$$

where

if 
$$\omega > k$$
,  $F = \frac{k}{(\omega^2 - k^2)^{1/2}} \sin 2\tau (\omega^2 - k^2)^{1/2}$   
if  $\omega < k$ ,  $F = \frac{k}{(k^2 - \omega^2)^{1/2}} \sinh 2\tau (k^2 - \omega^2)^{1/2}$   
if  $\omega = k$ ,  $F = 2k\tau$   
 $k = \frac{k_a + k_b}{2}$  = mean rate constant for the exchange process  
 $\omega = \frac{\omega_a - \omega_b}{2}$  = half chemical shift in radians s<sup>-1</sup>  
 $\tau = \frac{\pi}{2}$ ,  $\pi$  pulse interval.

In much of the experimentation described here a further simplification can be made if  $k\tau \ll 1$  and  $\omega \tau \ll 1$ :

$$[3] r_1 = \frac{2}{3}k\omega^2\tau^2.$$

This assumption is valid for  $\omega > k$  and  $k > \omega$  and applies in the region of small pulse intervals (short  $\tau$  limit). The time constants r result entirely from the exchange effect, and in the actual experiments account is taken of the additional natural relaxation processes expressed as the time constant  $1/T_{20}$ .

[4] 
$$\frac{1}{T_{2(CP)}} = \frac{1}{T_{20}} + r_1$$

where  $1/T_{2(CP)}$  = time constant of exponential decay observed in the Carr-Purcell experiment.

The application of spin-echo methods to the study of chemical exchange have been made previously by Reeves and co-workers (3, 4) and Luz and Meiboom (7). The latter workers derived an approximate expression for a multi-site exchange process for the limit of short pulse intervals and fast exchange,  $k \gg \omega$ . This equation will not be used here. A considerable volume of work by Gutowsky and co-workers has appeared while this present study was in progress (8–11). Insofar as the present study applies our original equations (1) to different rate processes, there is no overlap in the two parallel investigations. This paper should serve as an independent evaluation of the advantages and limitations of the spin-echo method to the study of chemical kinetics in the simplest cases (8–11).

#### Chemicals

## EXPERIMENTAL

N, N-dimethylnitrosamine was prepared by the reaction of dimethylamine hydrochloride and sodium nitrite in acid solution. The mixture was distilled to dryness and the distillate was treated with an excess of solid potassium carbonate. The nitrosamine appeared as a yellow oil which was further treated with potassium carbonate to remove water. The dimethylnitrosamine, b.p. 150–151 °C, was then doubly distilled. The overall reaction is given as:

 $(CH_3)_2NH + HNO_2 \rightarrow (CH_3)_2NNO + H_2O.$ 

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N,N-dimethyltrifluoroacetamide was prepared by the reaction of methyl trifluoroacetate and dimethylamine gas at -7 °C. The solution was then left at room temperature for 12 h and the product N,N-dimethyltrifluoroacetamide (b.p. 134–136 °C) was distilled out to 81% yield:

$$CF_{3}CO.OMe + NMe_{2}H \xrightarrow{-7.5C} MeOH + CF_{3}CO.NMe_{2}.$$
  
saturate

The steady state spectrum of pure N,N-dimethylnitrosamine was studied at 60 Mc/s on a Varian A60 spectrometer at temperatures in the range 125–195 °C. The exchange-modified spectrum was similar to that reported by Phillips (12) and Blears (13). The equations of Piette and Anderson (14) were used to derive rate constants from the line widths in the slow exchange limit.

#### Spin-Echo Apparatus

The spin-echo spectrometer operated at 40 Mc/s and was constructed in our own laboratories. It has not been reported previously, hence some description will be given here. The magnetic field was provided by a Varian 12 in. magnet shimmed for high-resolution experiments and with additional homogeneity trimming provided by a Varian V-4365 field homogeneity control unit. The non-spinning samples had a  $T_2^*$  (measured from the free induction tail) of 150 ms.

Figure 1 illustrates the generation of the Carr-Purcell pulse sequence. The r.f. generator, Fig. 2, consisted of a highly stable 10 Mc/s crystal oscillator, a pulse modulator stage, two frequency doublers, a 40 Mc/s driver stage and a push-pull final amplifier stage. The 10 Mc/s crystal was thermostatically maintained at



FIG. 1. Generation of the Carr–Purcell pulse sequence.

85 °C in a crystal oven. Careful interstage shielding was used to virtually eliminate 40 Mc/s leakage during the "pulse off" period. Phase coherent 40 Mc/s r.f. pulses were obtained by allowing the 10 Mc/s oscillator to run continuously while pulse-modulating the first doubler stage. A 90 degree r.f. phase shift during the  $\frac{\pi}{2}$ pulse was accomplished in the second doubler grid circuit by means of the Meiboom and Gill method (15). In this method a pulse, identical to the  $\frac{\pi}{2}$  modulation pulse, switches a back-biased semiconductor diode into its conductive stage; this procedure effectively places a phase-changing capacitor across the tuned circuit for the duration of the  $\frac{\pi}{2}$  pulse. The 90 degree r.f. phase shift during the  $\frac{\pi}{2}$  pulse served to minimize the effect of accumulative error which might occur in the width of the  $\pi$  pulses. The peak r.f. output power of this unit was approximately 250 W, giving a  $\pi$  rotation of magnetization in ~15  $\mu$ s.

The modulating pulse train was synthesized by the combined use of a Tektronix 545A oscilloscope, a Tektronix Type 162 waveform generator and three Type 163 pulse generators. A positive gate voltage was fed from the +Gate A terminal of the oscilloscope to the trigger inputs of two Type 163 pulse generators (modified to give pulse amplitudes of +90 V peak). These two generators produced the single  $\frac{\pi}{2}$  modulating pulse and the 90 degree r.f. phase shifting pulse. The  $\frac{\pi}{2}$  and r.f. phase shift pulses were thus synchronized with

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FIG. 2. Transmitter circuit.

the beginning of the oscilloscope sweep. To produce the modulating train of  $\pi$  pulses at times  $\tau$ ,  $3\tau$ ,  $5\tau$ , etc., the same + Gate A from the oscilloscope was used to gate a Type 162 waveform generator, producing a negative sawtooth train of variable frequency. This negative sawtooth train was used to trigger the remaining Type 163 pulse generator ("negative trigger" mode), producing the train of  $\pi$  modulating pulses. The

train of  $\pi$  pulses could be delayed from the  $\frac{\pi}{2}$  pulse simply by adjusting the "output pulse delay" control.

The  $\pi$  pulse repetition period was adjusted by means of the "pulse interval" control on the waveform generator (Type 162).

A Varian crossed coil probe was used and modified by appropriate changes of capacitors in the transmitter coil circuit to facilitate impedance matching. The probe can be used both for high-resolution and spin-echo experiments. The Varian probe, although quite inefficient in coupling r.f. energy from the transmitter coil to the sample, did give a homogeneous  $H_1$  field as indicated by the complete disappearance of the induction

tail after a  $\pi$  pulse in a  $\frac{\pi}{2}$ ,  $\pi$  pulse sequence. Receiver coil orthogonality and the leakage paddles used normally

for high-resolution studies could be adjusted to obtain excellent isolation between the transmitting and receiving coils. This adjustment was made such that the central portion of the r.f. pulse sensed by the receiver was negligible and only the high-frequency components (the leading and trailing edges) of the pulse were detected (as two small spikes). This optimal isolation condition facilitated quick receiver recovery time ( $\sim 3 \ \mu s$ ) and avoided inducing into the receiver coil large "ringing currents" which could distort the overall  $H_1$  from the transmitter coils. Such optimal conditions were not required for all of the present work, but were maintained as a matter of routine. The experiments described here were performed in a relatively homogeneous  $H_0$  field so that a continuous signal of detected pulses and echoes occurred.

The receiver was a modified L.E.L.-I.F. amplifier which was used as a 40 Mc/s broadband receiver (Figs. 3a, 3b). The preamplifier section used cascaded 5 842 stages. Manual control of receiver gain was provided by varying the grid bias of the third and fourth stages. Two means of signal detection were provided: ordinary diode detection and phase detection. In the phase detection mode, any attempt to draw more power from the transmitter oscillator to achieve frequency quadrupling resulted in loss of drive to the subsequent stages of the transmitter with loss of and varying power to the probe. An amplifying stage was used



FIG. 3a. Block diagram of receiver circuit.



FIG. 3d. Waveforms resulting from frequency multiplication showing respective amplitudes.

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FIG. 3b. Receiver circuit.

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FIG. 3c. Reference signal amplifier, multiplier, phaser, and attenuator.

to raise the power available from the transmitter oscillator to that required for frequency modulating (VI in Fig. 3c). To achieve efficient frequency multiplication with reasonably uniform output amplitude, two stages of frequency doubling were used (Fig. 3d). The original tube Type 6AH6 was used for all three stages; VI as a 10 Mc/s amplifier, V2 doubling to 20 Mc/s, and V3 doubling to 40 Mc/s. An additional advantage of this method is the minimizing of the risk of self-oscillation present when more than one stage is tuned to the same frequency. Reference to the paper by W. Gilbert Clark (24) was made to achieve good control of the phasing and attenuation for the system (Fig. 3c). In most cases the experiments presented here did not require the use of the phase detector. The maximum receiver gain was  $2 \times 10^6$  with a bandwidth of 3 Mc/s.

The echo amplitudes were photographed with a Polaroid oscilloscope camera on 3 000 A.S.A. film. Photographs were subsequently measured for echo amplitudes. Typical experiments are illustrated to indicate the performance of the apparatus. The  $\pi$  pulse interval was timed on a Hewlett Packard 522B electronic counter.

### RESULTS

Some attempt has been made in this work to investigate the precision of our  $T_2$  measurements in the Carr-Purcell experiment. The measurement is very sensitive to the resonance

condition (16), the inclusion of a  $\frac{\pi}{2}$  phase shift, and the homogeneity of the  $H_1$  field.

The resonance condition in such a homogeneous field is quite difficult to maintain. The oscillator frequency was certainly stable enough but small magnetic field drifts over a period of even 5 min necessitated readjustments. These were easily achieved by observation of the free induction decay with phase sensitive detection. The field was swept to give zero beat each time. The measurements of  $T_2$  values >5 s were appreciably shortened for slight field drifts from resonance. Satisfying the resonance condition is the most tedious part of the experimental procedure, and in future work, further precautions concerning this field drift will be taken. The magnitude of the magnetic field instability may be only 1 c.p.s. per minute but deterioration in performance can be detected after 15 min.

The accumulated error in echo amplitudes due to error in the width of the  $\pi$  pulse can also be corrected by working at certain off resonance conditions without a  $\frac{\pi}{2}$  r.f. phase shift in the first pulse (18). In the off resonance experiment we have to observe the condition that the  $\pi$ - $\pi$  pulse spacing is given by

$$2\tau = (2n + 1 \pm \frac{1}{2})T$$

where  $T = 2\pi/(\Delta\omega)_0$ ,  $2\tau$  is the  $180^{\circ}/180^{\circ}$  pulse spacing, *n* is an integer, and  $(\Delta\omega)_0$  is the angular frequency difference between the resonance condition and the applied frequency.

We found it satisfactory to work at about 4.5 Kc/s off resonance where the above condition could be satisfied for a range of  $2\tau$  between 1 and 10 ms. It must be noted that these off resonance experiments have far less flexibility in the pulse interval range and we found them much more difficult to perform when the pulse intervals were greater than 10 ms. All kinetic experiments reported here are repeated using both methods of obtaining  $T_2$ and agreement to  $\pm 5\%$  on  $T_2$  is claimed. The performance of the apparatus, while using the Meiboom and Gill (15) phase shift is shown in Fig. 4. The column of figures on the left of this figure indicates the pulse interval  $2\tau$ . Experimental Carr-Purcell trains are given in the next column corresponding to these pulse spacings. The computed  $T_2$  values in the third column vary, in this particular experiment performed on N,N-dimethylnitrosamine at 135 °C, from 10.1 s to 0.2 s. The time calibration for the decay can be obtained from the figures in column 4. The decays are all accurately exponential and with the large pulse spacing of 40.75 ms the individual echoes can be resolved.

A typical experiment such as that illustrated was performed at a series of temperatures

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Pulse Interval (2τ), (ms)	T <sub>2 (C.P.)</sub> (s)	Time Base (s⁄div.)	
1.30	10.1	2.0	
2.05	9,21	2.0	
2.58	6.30	2.0	
8.11	2.68	1.0	
10.24	2.03	1.0	
13.02	1.44	0.5	
20.48	0.72	0.2	
40.72	 0.20	0.1	

CARR-PURCELL TRAINS; N, N-DIMETHYLNITROSAMINE

FIG. 4. Representative Carr-Purcell trains at different pulse intervals.

for each of the two molecules under study. The results in the form of log  $1/T_{2(\text{GP})}$  versus log  $1/2\tau$  are plotted in Figs. 5 and 6 for N,N-dimethylnitrosamine and N,N-dimethyl-trifluoroacetamide respectively. The general shape for the complete dependence of  $T_{2(\text{GP})}$  upon pulse separation  $2\tau$  is best seen in Fig. 6. When  $1/2\tau$  is large the value of  $1/T_2$  approaches the natural value in the absence of chemical exchange. At large pulse separations  $(2\tau)$  the curve approaches the line width in the exchange-broadened steady state spectrum for the fast exchange limit. Both off-resonance and on-resonance results are plotted in Fig. 5. A considerable temperature dependence of  $T_{2_0}$ , the natural relaxation time in N,N-dimethylnitrosamine, can be seen in Fig. 5, which is very unusual because it indicates a shorter  $T_{2_0}$  as the temperature increases. This unusual behavior can be associated with the equilibrium

# $(CH_3)_2NNO \rightleftharpoons (CH_3)_2N-N(CH_3)_2 + 2NO,$

which produces small but increasing amounts of paramagnetic nitric oxide as the temperature is raised. This unusual temperature dependence of  $T_{20}$  is not observed in N,N-dimethyltrifluoroacetamide. The requirement of a rather more homogeneous field is important for N,N-dimethylnitrosamine because it is necessary to extend measurements to the relatively high temperature of 190–195 °C where diffusion processes are rapid.

The value of the rate constant k was obtained by use of eq. [2]. The experimentally observed value of r was obtained from eq. [4]. The value of  $T_{20}$  was equated to  $T_1$  measured in a separate experiment or was estimated by using the  $T_{20}$  indicated from Fig. 5 and 6 at infinitely fast pulse rates (a third method of estimating  $T_{20}$  from eq. [3] is described below.) An iterative FORTRAN program for an I.B.M. 7040 was used in which trial values of  $\omega$  and k were inserted and for the experimental values of  $(2\tau)$  the value of r was computed. These values of r were compared to experimental values and deviations were sensed by the computer. Changes in trial values of k were then made in order to minimize deviations from experimental values. The deviations were finally minimized by small changes in the choice of  $\omega$ . The best overall values of k to fit as many as 20 experimental determinations of  $T_2$  were found.

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FIG. 5. Dependence of  $T_{2(CP)}$  upon the pulse interval  $2\tau$  for N,N-dimethylnitrosamine: (a) on resonance, (b) off resonance. FIG. 6. Dependence of  $T_{2(CP)}$  upon the pulse interval  $2\tau$  for N,N-dimethyltrifluoroacetamide, on resonance: (a) 60.8 to 75.0 °C; (b) 80.3 to 95.3 °C.

It is of some interest to compare these values of k with those from the equation for the fast pulsing limit. Within the validity of eq. [3] the value of  $1/T_{2(CP)}$  was plotted against  $(\omega\tau)^2$  and a straight line was obtained for each temperature. The results for the two compounds studied are given in Figs. 7 and 8. Note that in Fig. 8, to avoid crowding, the values of  $1/T_2$  are plotted without a scale and each temperature is vertically displaced on the diagram. The value of  $1/T_2$  when  $(\omega\tau)^2 = 0$  gives the natural relaxation time  $T_{20}$  which may be used also in the curve-fitting procedure for the full dependence of  $1/T_{2(CP)}$  on



FIG. 7. "Short  $\tau$ " limit plot for N,N-dimethylnitrosamine: (a) on resonance; (b) off resonance.

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FIG. 8. "Short  $\tau$ " limit plot for N, N-dimethyltrifluoroacetamide, on resonance.

 $1/2\tau$ . The values of  $\omega$  chosen were those obtained in high-resolution experiments. A simple computer program was devised to obtain a least squares fit to the straight lines in Figs. 7 and 8 and the resulting slopes were converted to rate constants for each temperature. Then a least squares fit to the usual Arrhenius temperature dependence was used to evaluate the activation energy and frequency factor.

The important information derived from these experiments is the rate constant, k, and we compare the values of k for N,N-dimethylnitrosamine and N,N-dimethyltrifluoroacetamide in Tables I and II. The comparison with the high-resolution method

Т (°С)	$k^*$ off $\omega_0$ spin-echo	$k^*$ on $\omega_0$ spin-echo	k‡ A-60	$k^{\dagger}_{ m off \ \omega_0}$ spin-echo	k† on ω₀ spin-echo
$140 \\ 151 \\ 160 \\ 172$	2.52 7.56 11.8 33.0	$     \begin{array}{r}       1.97 \\       6.44 \\       8.73 \\       25.5 \\     \end{array} $	2.55 4.90 10.3 21.0	3.70 5.80 10.1 55.4	3.40 6.30 8.00 31.0
$172 \\ 183$	48.7	$25.5 \\ 27.4$	44.0	74.9	47.5

TABLE I Comparison of rate constants  $(s^{-1})$  for N,N-dimethylnitrosamine

\*Least square analysis of  $r_i \approx k \pm k \pm 2k(\omega r)^2/3$ . †Computer-calculated sinh<sup>-1</sup> F fit. ‡Steady state: Piette and Anderson (ref. 14).

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in Table I refers to our own determination. The agreement between the various methods is remarkably good except for the comparisons in Table II with the data of Woodbury and Rogers (23). In view of the small chemical shift difference in the molecule studied we would suggest that the rates determined by the spin-echo method in the present paper are better estimations of the true rates.

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Т (°С)	k* steady state	k† on ω <sub>0</sub> spin-echo	k‡ on ω₀ spin-echo
60.0	4.98	4.72	4.20
64.5		9.00	9.10
70.0	6.53	14.54	12.90
75.0	8.04	19.80	17.30
80.3	9.46	28.82	18.40
85.7	12.60	44.72	35.70
90.5	14.40	81.39	47 00
95.3	<u> </u>	103.11	\$8.70

			TAB	LE	II		
Comparison	of rate	constants	$(s^{-1})$	for	N.Ndimethyltrifluoroacetamide		

\*Steady state: Woodbury and Rogers (ref. 23). †Least square analysis of  $r_1 \approx k \mp k \pm 2k(\omega \tau)^2/3$  ( $E_{\mathbf{a}} = 20.6 \pm 1.4$  kcal). ‡Computer-calculated sinh <sup>-1</sup> F fit ( $E_{\mathbf{a}} = 18.5 \pm 2.7$  kcal).



FIG. 9. Activation energy determination for N, N-dimethylnitrosamine.

In Figs. 9 and 10 the activation energies are determined as least squares lines to all rate constant determinations. In Fig. 9 the origin of the  $T_2$  measurements is from both on- and off-resonance experiments for N,N-dimethylnitrosamine.\*

In Table III the best activation parameters are quoted for the two molecules studied.

# DISCUSSION

The spin-echo method for determining rate constants is now fairly well established and will serve as an independent check on high-resolution studies of rate constants. When both methods are in agreement a satisfactory set of activation parameters can be established for a given rate process. Unless this is the case, however, caution should be exercised in using the results. Abnormal frequency factors for simple hindered rotation barriers should be regarded with suspicion. In N,N-dimethyltrichloroacetamide, Gutowsky and Allerhand (19) were not able to obtain satisfactory agreement between steady state and spin-echo

\*In Fig. 10, the on-resonance activation energy determination is illustrated for N,N-dimethyltrifluoroacetamide.

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FIG. 10. Activation energy determination for N, N-dimethyltrifluoroacetamide, on resonance.

TABLE III Activation parameters

	E <sub>a</sub> (kcal/mole)	$A = (10^{12} \times s^{-1})$	S (e.u.)
N,N-Dimethylnitrosamine on resonance N,N-Dimethylnitrosamine off resonance	$21.9 \pm 1.6$ $22.9 \pm 1.7$	1.00 $6.04$	-2.93 - 3.92
Short $\tau$ limit Sinh <sup>-1</sup> F fit	$20.6 \pm 1.4$ $18.5 \pm 2.7$	$\substack{182\\6.90}$	$^{+4.22}_{-2.33}$

techniques. The case of the activation parameters for inversion in  $c-C_6D_{11}H$  (8) can be considered to be solved. The rate constants have been determined over a spectacularly large range of temperature and agreement with the high-resolution studies is now complete (20, 21). A quantum mechanical theory of the spin-echo experiment on an exchanging system has now been given (22). The primary disadvantage of the spin-echo method is its lack of selectivity. Usually all nuclei of one type are in or near the resonance condition during pulses.

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