

# A METHOD OF SELECTIVE MEASUREMENT OF SPIN-LATTICE RELAXATION TIMES OF CHEMICALLY-SHIFTED PROTONS

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An experimental technique for measuring distinct relaxation times of chemically-shifted groups of nuclei is proposed. The very simple and rapid procedure is based on only two passages through resonance applying a two-level rf field in a high resolution nmr spectrometer. Verifying measurements for toluene, methanol and ethanol were performed.

## 1. Introduction

Investigations of relaxation time spectra of chemically-shifted nuclei are essential to the understanding of the dynamics of molecular motion in liquids. Various high resolution methods permit determinations of distinct spin-lattice relaxation times of chemically-shifted protons recurring to adiabatic fast passage (Nederbragt and Reilly 1956, Bonera *et al.* 1960, Powles 1963), spin echo (Alexander 1961, Kamei 1967), saturation-recovery (Van Geet and Hume 1965) or adiabatic passage with sampling technique (Anderson, Steele and Warnick 1967). However extensive studies of molecular dynamics have not been undertaken to date although their importance has long been recognized. To facilitate this, a null method is proposed simplifying the procedure of measuring distinct spin-lattice relaxation times and involving only two passages through resonance at strong and weak rf field.

## 2. Principle of the method

The method makes use of adiabatic fast passage, for which the conditions are:

$$\frac{1}{T_2} \ll \frac{1}{H_1} \left| \frac{dH}{dt} \right| \ll |\gamma| H_1. \quad (1)$$

Let us consider two passages following one another after a time interval  $\tau$ . The first adiabatic fast passage inverts the magnetization vector  $M_0$ . Since, after inversion, magnetization increases again from negative values through zero to positive values, the time interval  $\tau$

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between the two passages can be chosen in a manner which makes the signal of the second passage vanish.

From the equation

$$M_z = M_0 \left[ 1 - 2 \exp \left( - \frac{\tau}{T_1} \right) \right] \quad (2)$$

one obtains the known condition permitting the determination of  $T_1$ :

$$\tau = T_1 \cdot \ln 2. \quad (3)$$

It is worth noting during the second passage the sample can be submitted to a weak rf field only, condition (3) still remaining valid (Anderson 1960). This was the idea put in practice in the present method of measuring relaxation times of various groups of protons. In contradistinction to the null method used by Bonera, De Stefano and Rigamonti (1962) involving only one-level strong rf field this method involves two-level strong and weak rf field. Using a strong rf field causes broadening of the NMR lines thus making impossible the precise, selective measurement of relaxation times of a distinct groups of a protons. One of the essential conditions for preserving high resolution consists precisely in the use of a weak rf field — and this takes place in the second passage of the described method.

### 3. Details of the spectrometer

A high resolution conventional Bloch type spectrometer constructed in this Laboratory was adapted to measurements of distinct relaxation times of chemically-shifted proton groups. A general block diagram of the spectrometer with attachment for measuring  $T_1$  is shown in Fig. 1.

The magnetic field is produced by a permanent magnet (Trüb-Täuber). The transmitter coil in the probe head is supplied by a 25 MHz quartz generator with stability increased by control of the crystal temperature. Most of the leakage is mechanically reduced; the insignificant, remaining part is compensated electronically with a bridge. The NMR signal amplified by means of a preamplifier and receiver, after phase-sensitive detection is displayed on a cathode-ray oscillograph. The waveform generator (Servomex L. F. 51 Mk II) provides the appropriate pulses by a cathode follower to the coils modulating the magnetic field and simultaneously controls the oscillograph time base. For providing a sufficiently high level of rf field a power amplifier was constructed (Fig. 2).

The output of the latter is passed by means of a symmetric cable of capacity 6 pF to the receiver coil in the probe head. The amplification of the first three stages (valves  $V_1$ ,  $V_2$  and  $V_3$ ) is small. Their chief aim is not to provide amplification but to improve the blocking effectiveness of the next circuits (valves  $V_4$  to  $V_7$ ). The circuit on diodes ( $D_1$ — $D_4$ ) serves for transforming the rectangular pulses C (see Fig. 3) from the waveform generator into pulses with negative polarity used for blocking the rf power amplifier. Similar circuits transform the rectangular B pulses for blocking of preamplifier and receiver. The switch P permits continuous blocking of the rf power amplifier enabling the observation of hr NMR spectra in stationary conditions.

#### 4. Experimental procedure

The procedure requires generation of the coherent waveforms shown in Fig. 3.

Waveform A was used for symmetric modulation of the magnetic field and for controlling the oscillograph time base. The two half-periods were equal:  $\tau_1 = \tau_2 = \tau$ . Waveform B served for blocking the preamplifier and receiver, and waveform C for blocking the power amplifier.

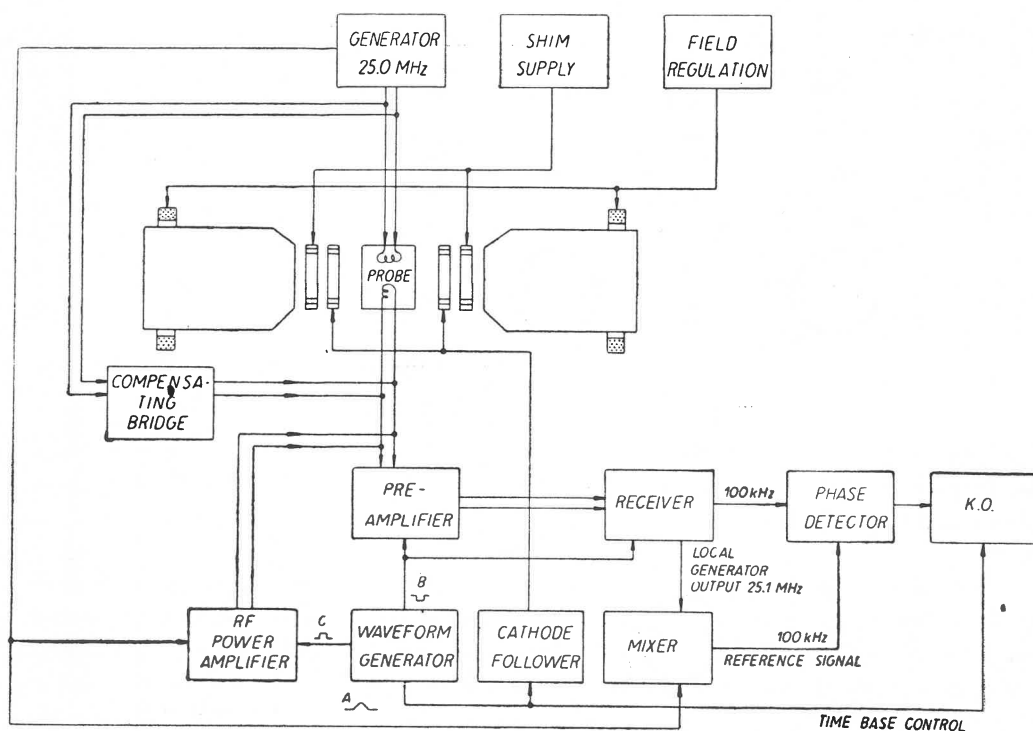


Fig. 1. Block diagram of spectrometer, together with  $T_1$  — attachment

As stated, the present method involves but two passages through resonance. When the time interval  $\tau$  between the two passages found by testing is equal to  $T_1 \ln 2$ , the NMR signal at the second passage vanishes. Let us now consider the procedure in more detail.

At the moment  $t_0$ :

1. Waveform A begins to modulate the magnetic field, the oscillograph time base runs in synchronism with modulation (the spot on the oscillograph screen starts moving from left to right),

2. Waveform B blocks the valves of the preamplifier and receiver for the duration of the first half-period  $\tau_1$ .

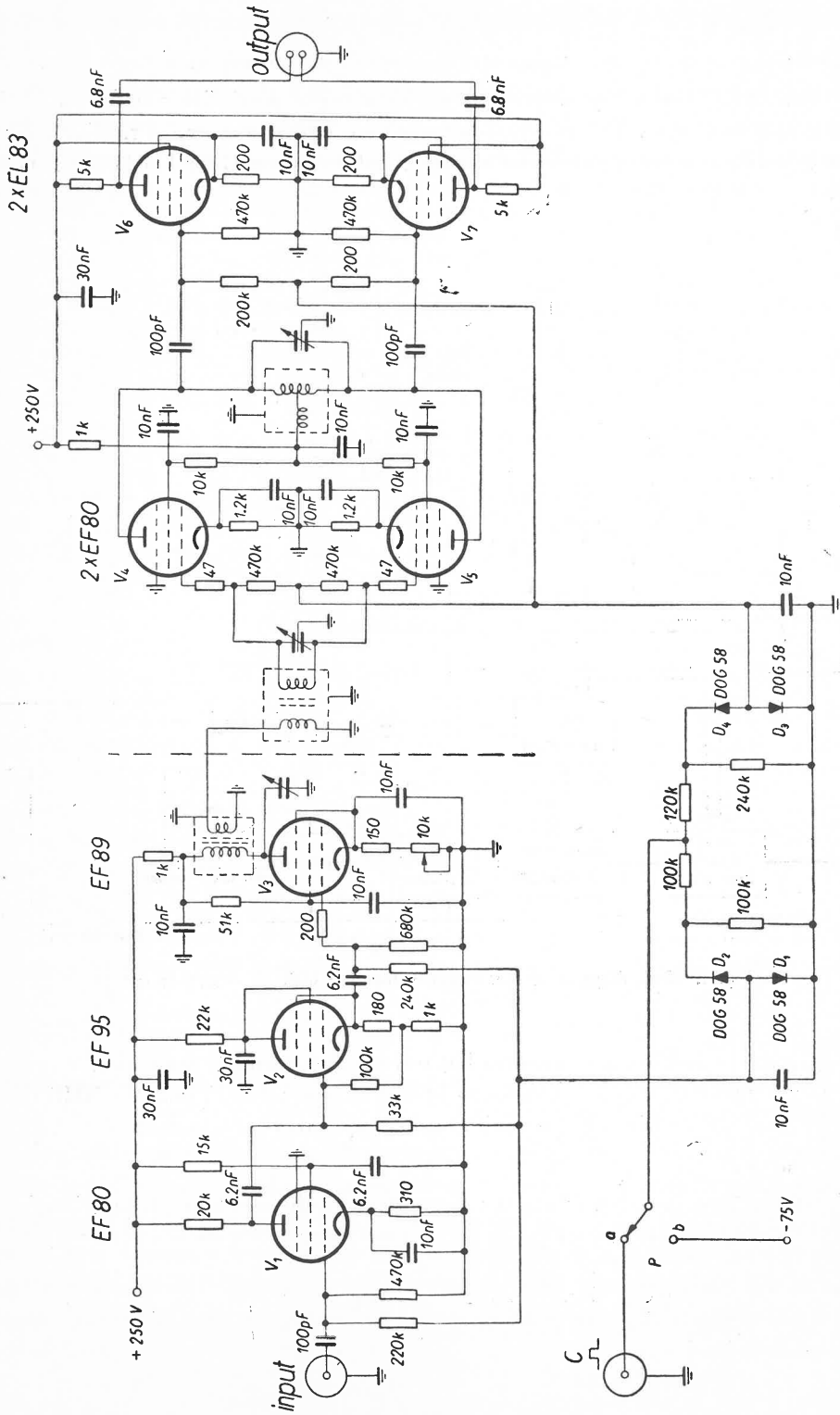


Fig. 2. Diagram of rf power amplifier

3. Waveform C drives to operation the rf power amplifier for the duration of the first half-period  $\tau_1$ .

During the first half-period the sample subjected to a strong rf field passes through resonance (adiabatic fast passage); the NMR signal, however, is not visible on the oscillograph screen due to the simultaneous blocking of the preamplifier and receiver (pulses B). Thus, the advantage of the method consists in an important simplification of the operating

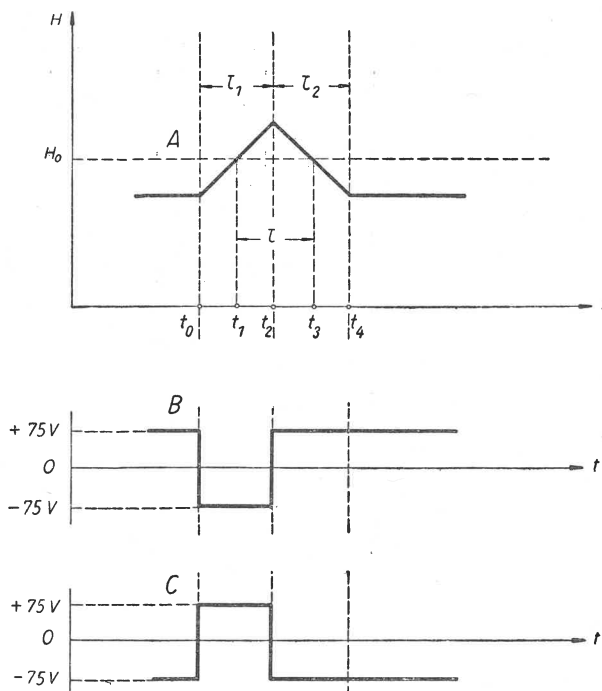


Fig. 3. Waveforms used for measuring  $T_1$

procedure making unnecessary much troublesome work related with the compensation of leakage and the balancing of the receiver system.

At the moment  $t_2$ :

1. Waveform A modulates the field in the inverse direction (the spot on the oscillograph screen begins to move from right to left),
2. Waveform B drives to operation the preamplifier and receiver valves,
3. Waveform C blocks the valves of the rf power amplifier.

For the duration of the second half-period  $\tau_2$  the sample is subjected to the weak rf field only. At resonance ( $t_3$ ), the NMR signal can be observed, provided  $\tau \neq T_1 \cdot \ln 2$ . The line in the NMR spectrum for which  $\tau = T_1 \cdot \ln 2$  vanishes. The time  $\tau$  is obtained directly from waveform generator reading. At the moment  $t_4$  the state is that preceding the moment of time  $t_0$ .

## 5. Measurements

Verifying measurements of  $T_1$  for toluene, methanol and ethanol were performed and the results are compared in Table I with those of other authors.

TABLE I

Liquid		Present results	Literature values				
			<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
Toluene	$T_1\text{C}_6\text{H}_5$	16 sec 24°C	16 sec 25°C	15 sec 24°C	16 sec 20°C		
	$T_1\text{CH}_3$	9 sec 24°C	9 sec 25°C	8 sec 24°C	8.3 sec 20°C		
Methanol	$T_1\text{OH}$	6.5 sec 24°C		7.5 sec 22°C			4.7 sec 25°C
	$T_1\text{CH}_3$	6.5 sec 24°C					4 sec 25°C
Ethanol	$T_1\text{OH}$	2.7 sec 22°C				2.8 sec	
	$T_1\text{CH}_2$	3.9 sec 22°C				4.0 sec	
	$T_1\text{CH}_3$	4.5 sec 22°C				5.7 sec	

*a* — Nederbragt and Reilly 1956.

*b* — Bonera *et al.* 1960.

*c* — Powles 1963.

*d* — Van Geet and Hume 1965.

*e* — Powles and Neale 1961.

For toluene, the results obtained in measuring relaxation times are in good agreement with published data. For methanol, the distinct values 4.7 sec and 4 sec (at 25°C) from graphs of  $\log T_1$  vs. temperature obtained by Powles and Neale (1961 b) are much lower than those measured by the present method. The values are identical for the two groups  $T_1=6.5$  sec. Bonera *et al.* (1960) suggest however that the two times differ but slightly — they obtained a single value of 7.5 sec (at 22°C). For ethanol, the measured relaxation times for the groups OH and  $\text{CH}_2$  coincide with those of Van Geet and Hume (1965), whereas our value for the  $\text{CH}_3$  group is much lower. The error of measuring relaxation times by the present method amounted to 5 per cent.

## 6. Conclusions

The above described method is well adapted for determining the distribution of relaxation times of sufficiently well resolved proton groups in NMR spectra. The method permits measurements of times  $T_1 \geq 0.3$  sec. Measurements of longer and longest relaxation times

set no obstacles, notwithstanding the shift in zero level due to unbalancing of the bridge. Neither does a possible nonlinearity of the receiver system affect the error. The measuring procedure as such is very simple and can be performed quite rapidly. Another advantage of this null method consists in the fact that the signals need not be recorded with an automatic recording device or photographed from the oscillograph screen. The method moreover admits the construction of simple attachments (Pająk, Jurga and Jurga 1969) for commercial high resolution NMR spectrometers.

The method is at present applied for extensive studies of relaxation time distributions in organic molecules with the aim of obtaining better insight into the dynamics of molecular motion. Results obtained for toluene and various other compounds involving methyl groups will be published shortly.

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