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Measurement of Molecular Tunneling by Using Nuclear Magnetic Resonance Technique

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Abstract

The molecular dynamics behaviour of tert-butyl groups were investigated by NMR tools. The methyl group (CH3-C) provides one of the simplest system for studying motion in both the quantum and classical regimes. The rigid triangle of protons is free to rotate only about a central axis perpendicular to its plane. Both the tunnel splitting and spin lattice relaxation T1 and the hoping rate depend upon the height and the shape of the hindering barrier to the methyl rotation. The goal is to relate the dynamics behaviour of tert-butyl group and molecular environment for number of samples containing tertiary-buty groups. The results suggest the important of collective motion of methyl group in tert-butyl.

Keywords: susceptibility, annealing treatment, Invar alloy, Curie temperature (Tc)

1. INTRODUCTION

The nuclear magnetic resonance tunneling (NMR) and spin-lattice relaxation are a powerful technique for the investigation of atomic and molecules motion in tret-butyl groups like CH3 [1]. NMR is sensitive to motion of proton spins through the dipole-dipole interaction. Many experiments can be performed using NMR to describe the dynamics of rotation lead to understand the behavior of the angular anisotropic of the sample under investigation for both states ie (the intramolecular and intermolecular in the solid state [2,3]. At low temperature the measurement of tunnel splitting for CH3 give us accurate values for both the magnitude and shape of the potential barrier along with predictions for the hierach of torsional state within the barrier, also at low temperature the motion of the protons of the tret-butyl can usually be neglected. The relaxation due to the dipolar interaction, is much more rapid than spin-lattice relaxation. All protons of the specimen relax as a single system.

The spin lattice relaxation, T1 results are used to evaluate tunnel frequencies in other cases. The results suggest the important of collective motion of methyl groups in tert-butyl. On the other hand the dynamics are described theoretically by invoking. Photon interaction explicitly and on the other hand the role of the phonons is merely that a thermal bath to establish and maintain Boltzmann population within the torsional ladder of levels. Here we report and model the temperature dependence of nuclear (proton) spin lattice relation time, NMR relaxation measurement in tert-butyl-nitrite, tert-butyl mrthylether, tert-butyl peroxide pivalic acid (2,2 dimethyl propionic acid all this samples are included here as speciments of how the relaxation of (CH3)3 changes. In this work our aim to find the behaviour of tert-butyl group when it is in contact with different atoms. As a result the comparison between the motional spectrum of difference (CH3)3 materials will be related to the molecular structure. On the other hand the experimental result for all materials was a nother test for validity of S. Clough et al's model [4,5]. The reorientation rate versus temperature T1 is calculated by using the measured tunnel splitting as in input parameter and compared with experimental values. NMR is a powerful technique for the investigation of rotational tunneling of small molecules or molecular group like CH3 [6]. Also NMR is sensitive to motion of proton spins through to dipole-dipole interaction.

2. EXPERIMENTAL PROCEDURE

2-1 Sample Preparation

Most of the samples studied were liquid at room temperature, Degassing a sample is of prime importance in relaxation studies. We used a procedure to eliminate paramagnetic oxygen degassing under a vaccum. The equipment used in shown [7]. A freeze-pump thaw cycle began by cooling sample contained in cell number 3 and by opening values V3 and V5 until the pressure fell to about 10^{-15} Torr. V3 was then closed and the nitrogen trap number 2 was removed until the sample in cell number 3 and reached room temperature. The freeze-pump-thaw cycle was repeated four or five times until the sample completely distilled. A small volume of the distilled sample was then transferred to cell number 1 and the glass sample tube was sealed off under Vaccum (10^{-15} Torr).

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2-2 NMR Measurements

Measurements of spin lattice relaxation were made by using the saturation-recovery method described in [8] at a resonance frequency of 21 MHz. In this work two pulsed N.M.R. spectrometers were used. A spin lock spectrometer operating at 26 MHz was used for the low field experiments and the pruker pulsed NMR spectrometer which operator at 21 MHz was used for measurement of proton spin lattice relaxation T1 had been done by using the field cycling process employed to estimated the spin relaxation in level crossing region. The equilibrium magnetization was saturated by a single (90˚ pulses after that the magnetic then switched at period of (0.3 T per second) to ensure complete recovery for inspection field the best way for that the region interact field and the recovered magnetization (Mr) measured by repeated a 90 pulses cycle increasing the inspection field methodically at each step to race out tunneling spectra. The specimen temperature was maintained at atmospheric pressure. The preparation period of specimen at high magnetic field (topically 5T) was prime important made prior at each scan in the manner Clough at al technique [9, 10].

3. RESULT

3-1 Spin-lattice relaxation T1 versus temperature.

Spin lattice relaxation time of terty-butyl proceeds mainly via dipolar coupling or is dominated the quadrupolar interaction. Both are modulated by the motion of the methyl group about their symmetry axis rotation and from the rotation of the whole tery-butyl group about axis passing through C-Cl bound. The minimum of relaxation time due to the reorientation of tert-buytl around the C3 axis. From NMR investigation for tery-butyl compounds assuming the motion are activated and independent of each other. The result of T1 measurement can be analyzed in terms of the classical BLocmbergan-purcel, pound (BPP) theory for nuclear spin lattice relaxation [11]. From Haupt [12] modified of (BPP) extra components in the spectral density function related to the tunneling of CH3 can be found. Calculation from Fig. (1) shows the value of T1 minima is 146.8k and that is associated with measured tunnel frequency of 0.7╳105 Hz which corresponds to three-fold barrier height (3d) of (200k).

The most common way of measuring the methyl group reorientation rate is to study the temperature dependence of proton spin-lattice relation time T1. The T1 versus temperature curve develops a secondary minimum to the high temperature side of the main one as show in Fig. (2). This has been studied by H. Haupt [12], who has suitably modified the (BPP) theory to give a more complete expression and precise description of the connection between two parameters ie (reorientation rate and spin lattice relaxation time T1. As follow:

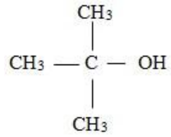
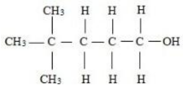
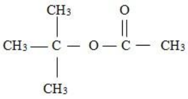
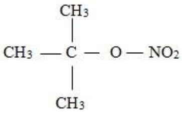
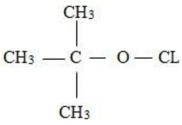
$$\frac{1}{T1} = C_1\left[\frac{\tau}{1+\omega_0^2\tau^2}+\frac{4\tau}{1+4\omega_0^2\tau^2}\right] + C_2\left[\frac{\tau}{1+(\omega_0-\omega t)^2\tau^2}+\frac{4\tau}{1+(2\omega_0-\omega t)^2\tau^2} + \frac{\tau}{1+(\omega_0+\omega t)^2\tau^2}+\frac{4\tau}{1+(2\omega_0-\omega t)^2\tau^2}\right] \quad \ldots\ldots..(1)$$

Where ωt/2π is the tunneling frequency, C1,C2 are the lattice sums of proton dipole-dipole matrix elements where C1 corresponds to the transition Ea → Eb which give a field dependent Ea → Eb minimum in T1 reflecting the transfer of nuclear Zeeman energy. The C2 term corresponds to transition A → E which give a field independent A → E because the Zeeman energy is only a small part of the total energy transferred in these transitions. Fig.(2) shows the spin lattice relaxation time versus temperature we observe two minima. These are clearly observed at 74.7 and 148.8k. in such cases the two minima in T1 relate to the two chemically distinct end-of-chain CH3 groups tert-butyl methylether is an interesting sample in its relation behaviour. For this sample barrier height was 1100k we have predicates the tunnel splitting is 0.6╳107 Hz as height 2050k. the temperature dependence of spin lattice time T1 for tert-butyl peroxide shows in Fig.(3) the T1 minimum at 163k. Fig.(4) show the same story of 2,2 dimethyl propionic acid (CH3)2COOH and it's minimum at 165k. Fig.(5) shows employing the correlation of Clough et al. the results in Fig.(1) to Fig.(4) have been interpreted to provide estimates the tunneling frequency for each sample.

3-1 The low field measurement in tertiey-butyl group sample

The values of tunneling frequency for pivalic acid and tert-butyl peroxide (2,2) dimethyl propionic acid had been measured by using low field N.M.R technique. Figure (6-8) presents the data recorded by level-crossing N.M.R spectroscopy. Each one is a plot of magnetic field in mT versus the recovered magnetization in arbitrary unites. A summary of tunneling frequency of these samples is shown in table (1).

Table 1: Show the tunneling frequency values, T1 minimum and high barrier values

Sample	Structure Formula	T min [k]	νt Hz predicted	νt KHz measured	V3 [k]	E^a [k]
Tert-butyl alcohol	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$	163	8×10^4	170±2 127±2	1850	770
2,2, Dimethylpent anol	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	74.7 148.8	0.6×10^7 0.5×10^5		1100 2050	577 1211
Tert-methyl acetate	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-\overset{O}{\overset{\Vert}{C}}-CH_3$	114.3	11×10^6		1600	1240
Tert-Butyl nitrate	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-NO_2$	146.8	0.7×10^5		2000	1180
Tert-Butyl	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CL$	165	8×10^4	382±5 112±5 90±5	1780	480

From it one can see the tunnel frequency and barrier height changes. Both changes are presumed to be due to the different in crystal field for different sample. The measurements of tunnel splitting associated with the low temperature T1 have consequently shown the methyl groups are responsible for spin-lattice relaxation in this region, for that reason the barrier heights have been accurately measured. Fig.(6) a,b shows six typical set of results for pivalic acid sample for irradiation frequencies of 500MHz, 550MHz, 600MHz, 700MHz, 800MHz and 850MHz respectively. The all show a clear Δm=1 transition near 14 mT this transient occurs at field given by B=w/2π [13] with a side band at lower field.

4. DISCUSSION OF T1

The effect of methyl group rotation (GH3) with the tert-butyl groups was studied as a function of temperature. The spin lattice relaxation is fairly strongly hindered as is indicated by the relatively high temperature at the which the T1 minimum occurs due to a more wedly hindered methyl group. In Fig. (2) is a plot of T1 versus and 29.8k, that behavior indicate the existence of two sets of methyl group with different potential barrier heights. The low temperature minimum(29.8k) is associated with predicated tunnel splitting of 0.6×107 Hz. The high temperature minimum 150.4k is associated with the predicted tunnel splitting of 0.3╳105 Hz.

The value of T1 at the minimum shows that in most cuses rotation is fast compared with rotation of the whole t-butyl group, but the case of t-butyl methyl ether is anomalous [9].

The low field NMR dute of the tunnel psliting for methyl group in tertiary butyl series reveals tunnel splitting in the different energy range. The tunneling frequency of these samples is shown in table (1). From it one can see the barrier height and tunnel frequency changes. These changes in the barrier height and the tunnel frequency are presumed to be due to the difference in the crystal field for different samples. Tunneling data suggest that for each molecule one in methyl group (CH3) is in an essentially low barrier environments and one in a high. Also the splitting observed is due to methyl group in high barrier environment we have observed the breadth of the tunnel spectrum is attributed as a results of differences between the methyl crystal sites for different methyl sites per unit cell is believed to be small.

5. CONCLUSION

In this work we interpret the T1 minimum versus temperature data by using the Clough et al's theory which concluded the thermal bath model for the motion of the methyl dynamics. It has been demonstrated to be very good. Measurements of the protons spin lattice relaxation T1 for some samples contains tert-butyl group [$C(CH_3)_3$] and their three constituent methyl group (CH_3) at Larmar frequency of $w/2\pi$= 21MHz. were subsequently proved to be accurate by tunneling spectroscopy. in studying a series of materials to prove the fact that methyl reorientations is superimposed on the rotation of the whole group and these studies aid new ideas of the nature of the molecular environment of the methyl group. The purpose of chosen samples to opint out a few interesting and important features of the nuclear spin-lattice relaxation as a function of temperature. Experimental work shows the value of T1 minimum in most cases rotation is fast compared with rotation of the whole t-butyl group, but the case of methyl ether is anomalous. During this work the temperature dependences of proton spin-lattice relaxation time from 55-245k is reported for tert-butyl peroxid acid and dimethyl propionic acid whose tunneling frequencies have been measured very precisely. The dominant fact emerging from this work is that tert-butyl has characteristic T1 minimum (□165k). the CH3 tunnel frequency is expected to be about 100 KHz and our results confirm this. the important thing in this study is that the coupling between the groups is expected to be important and evidence for this is complex nature of the tunneling spectrum. Some samples exhibit lower T1 below 165k and we attribute this behaviour of methyl group will lower hindering barriers and rotation as a whole group and that confirmed by the presence of weaker minimum at 165k.

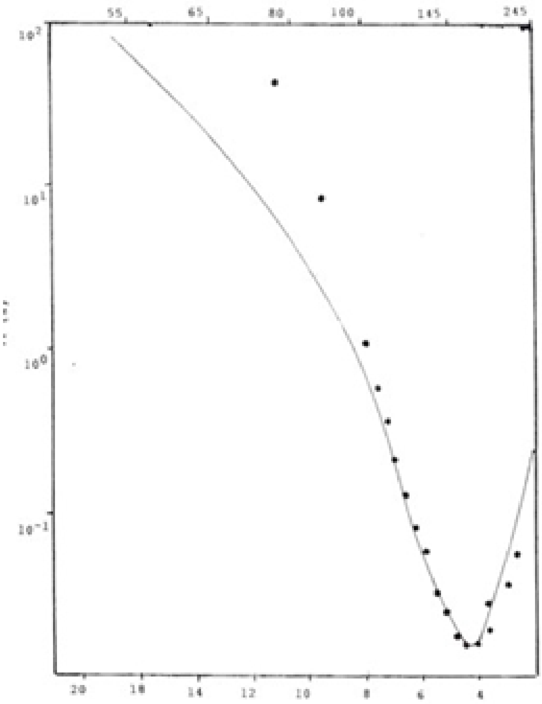


Fig. 1. The temperature dependence of T1 in Tert- butyl alcohol at NMR Frequency 21 MHz

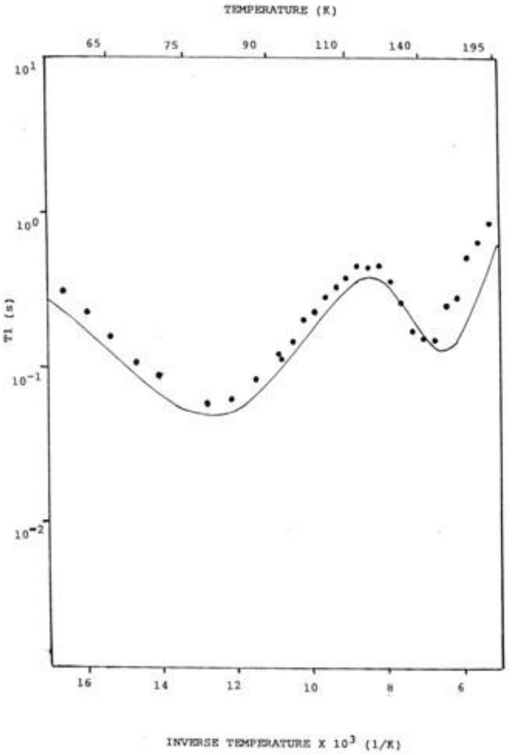


Fig. 2. The temperature dependence of T1 in 2,2, Dimethyl pentanol at NMR Frequency 21 MHz.

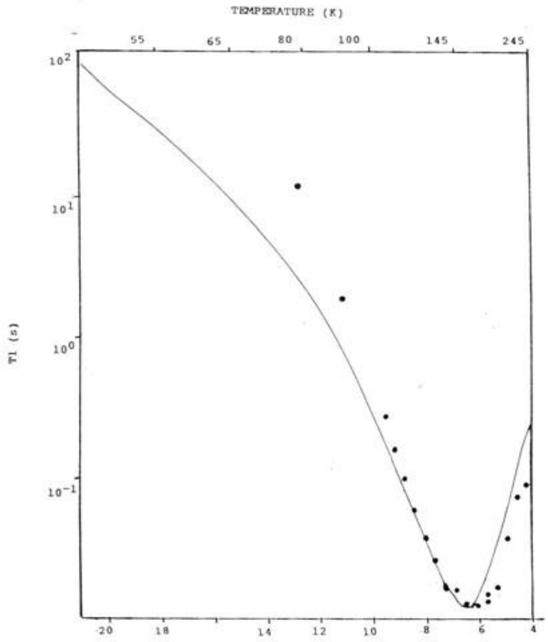


Fig. 3. The temperature dependence of T1 in Tert- methyl acetate at NMR frequency 21 MHz.

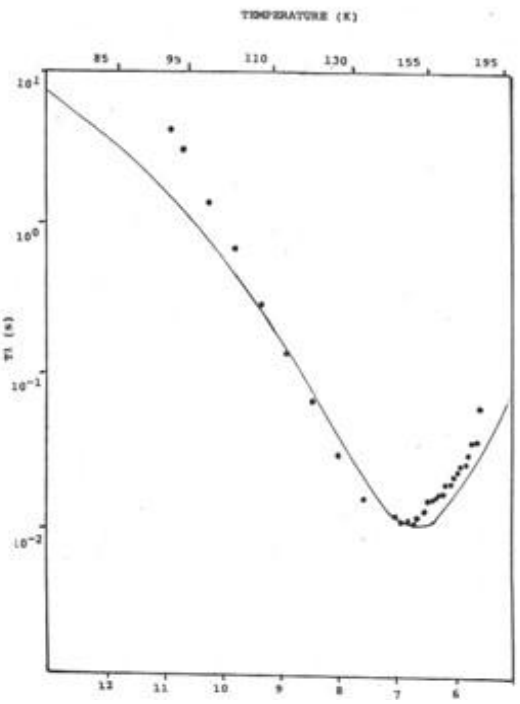


Fig. 4. The temperature dependence of T1 in tert-butyl -nitrite at NMR Frequency 21 MHz.

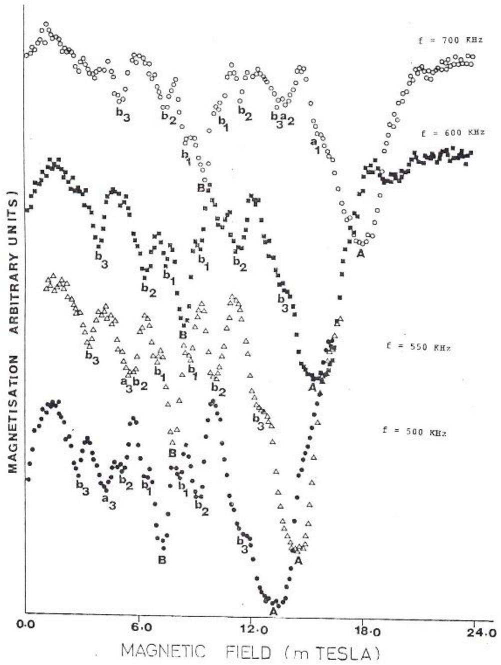


Fig. 6(a). The low field NMR spectra (4k) of pivalic acid (2,2 dimethyl propionic acid recoded at a veriety of frequency. See text for details.

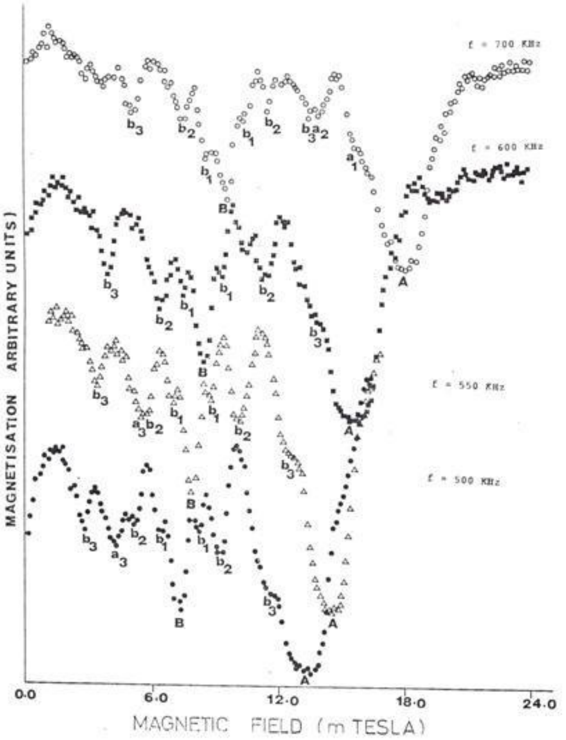


Fig. 5. The low field NMR spectra (4k) of Tert- Butyl hypoclorid recoded at a veriety of frequency. See text for details.

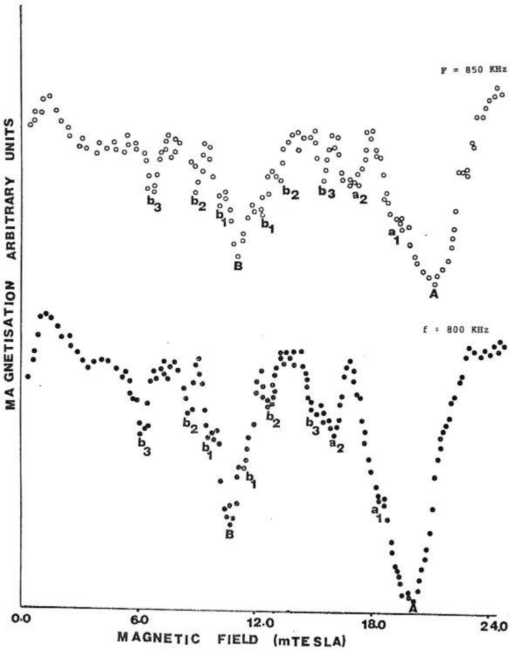


Fig. 6(b). The low field NMR spectra (4k) of pivalic acid (2,2 dimethyl propionic acid recoded at a veriety of frequency. See text for details.

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