RESEARCH ARTICLE OPEN ACCESS

Protons Relaxation and Temperature Dependence Due To Tunneling Methyl Group

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ABSTRACT
Tunneling frequency and temperature dependence of proton spin lattice relaxation time T1, are depend upon the height and the shape of the hindering barrier of methyl rotation and carry information on the group is molecular environment are reported for some samples containing tertiary-butyl group.The temperature rang was 4-300k.Data has been analyzed to provide estimates for the magnitude of the three fold potential barrier to reorientation of all methyl groups in these materials. At low temperature the motion of the tertiary-butyl protons can usually be neglected. All protons of the samples relax as a single system.In one or two cases tunneling is observed for the first time in Tert-butyl. The T1 results are used to evaluate tunnel frequency in other cases. The result suggest the importance of collective motion of methyl group in tert-butyl

I. INTRODUCTION

The methyl group has been used as the ideal system for study of atomic and molecules motion in the solid state. The reasons for the choice have been discussed by a number of authors and for example in review by press and reference [1].

The tunneling rotation of CH_3 is usually determined by the molecular environment of the group which sets up potential barriers to the rotation. Measurementof the CH_3 tunnel splitting barrier at low temperature provides us with accurate values for the magnitude and the shape of the potential barrier along with predictions for the hierarch of torsional state within the barrier.

The latters have been approach of Clough et al [2, 3]. Here the phenomenological model of S.Stciskal and Gutowsky [4]has been modified and the quantum mechanical principle formalized to provide a single parameter theory in which the only variable is the barriers height. This is in contrast to theories which introduce.

Phonon interactions explicitly in which many unknown coupling are invoked [5]. The samples chose for this investigation are Tert-butyl alcohol, 2,2 Dimethylpentanol, Tert methyl acetate, Tert-Butyl nitrate and Tert-Butyl hypocloridare included here as example of how the relaxation of $(CH_3)_3$ changes, it is our aim to find the behavior of tertiary butyl group when it is in contact with different atoms.

In this work the temperature dependence of proton spin lattice relaxation (T1) for all samples studied in order to provide a further test of the validity of Clough et al model. The (N.M.R) technique was used to perform the experimental measurement.

II. EXPERIMENTAL DETAILS

Measurement of the CH_3 tunnel splitting using dipole-dipole driven N.M.R experiment, measurement of proton spin lattice relaxation T1, were made on pulsed N.M.R, spectrometer system which operates at 2l MHz.A saturation- recovery technique was employed and recovered magnetization was observed to grow exponentially with experimental error. For T1 experiments the temperature between room temperature and 4kcould be reached by pumping helium from the bath surround the superconducting magnet into a dewar, vessel running through its central bore. A needle valve controlled the flow rate. A period of sample preparation at high field (Typically 5T) was made prior to each scan in a manner of techniques describe to be Clough et al. [6, 7].

III. RESULT AND DISCUSSION

3-1 The low field measurement in tertary-butlyl group sample.

The low field N.M.R data for this series are shown from figure (1-5). Each one is aplotof magnetic field in mT versus the magnetization is arbitrary unity. A summary of the tunneling frequency of these samples is shown is table (1). From it one can see the barrier height and tunnel frequency changes. These change in the barrier heights and the tunnel frequencies are presumed to be due to the different in crystal field from different samples.

3-2 T1 versus Temperature

The T1 measurement will be presented and compared with the predication of well-established correlation between splitting of the ground torsional state ($\hbar$, ν_t) and temperature at

which T1 is a minimum and the well be connected to the molecular environment of methyl group in the unit cell.

Fig (1- 5) display the results of measurement upon the samples in Fig (2). We observed two minima. These are clearly observed at 74.7 and 148.8 K. this is an interestingsample in its relaxation behavior. The T1 at the minimum in Fig (2) is small enough in indicate that almost all the protons in sample are involved in the motion. In some samples at a low temperature minimum occurs due to a morewedlyhindered methyl group.

The data of Fig (2) is remarkable because the t-butyl minimum is very shallow. The only possible explanation for this that the t-butyl group is already rotates as a whole at low temperature. There by contributing to the low temperature minimum when the methyl groups begin to rotate within the t-butyl group. The dipole-dipole interactionis already time dependent due to the rotation of the t-butyl group at a whole cross relaxation due to the dipolar interactions is still much more rapid than spin-lattice relaxation [8]. Consequently all protons of the samples relax as a single system. If all protons of a single molecule are relaxed by a single methyl group, the relaxation is slower than if the group were isolated see Fig (1) and Fig (2).

IV. CONCLUSION

In this paper measurement of dependence (T) of the protons spin lattice relaxation rate (T1) in the Tert-Butyl Alcohol 2,2 Dimetylpentanol, Tert-methyl acetate, Tert-Butyl nitrate and Tert-Butyl hypoclorid at a Larmer frequency of $W/2\pi$=21 MHz. These studies aidin the investigation of the nature of molecular reorientation. The chosen our experimental work in these samples to point out a few interesting and important features of the general problems of the proton spin-lattice relaxation in molecules solid as the temperature are varied.

The temperature of the T1 minimum are quits similar to other CH_3 group attached to SP^3hydridised atoms. The value of T1 at the minimum shows that in most cases rotation is fast compared with rotation of the whole t-butyl group, but the case of Tert-methyl acctate is anomalous. We interpret the T1 minimum versus temperature data with the theory. Clough et al. this is used to estimate the tunnel frequency for the t-butyl series and other samples.

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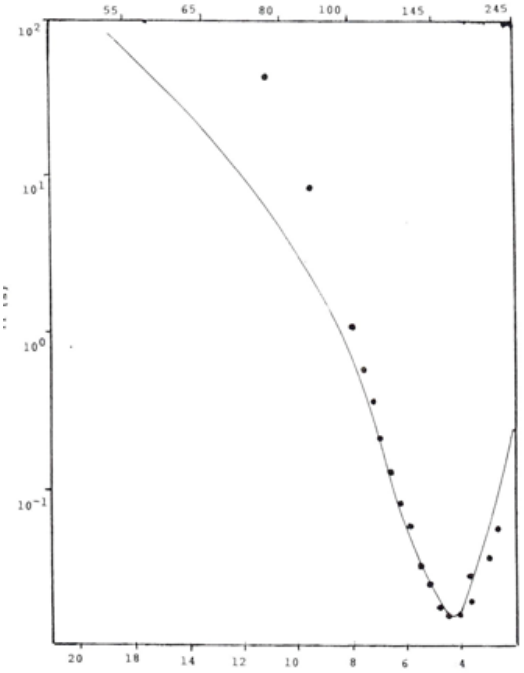


Fig. 1 The temperature dependence of T1 in Tert-butyl alcohol at NMR Frequency 21 MHz.

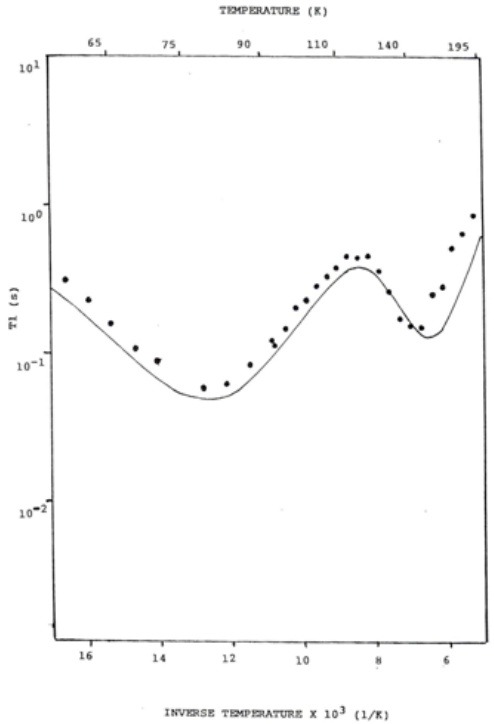


Fig. 2The temperature dependence of T1 in 2,2, Dimethyl pentanol at NMR Frequency 21 MHz.

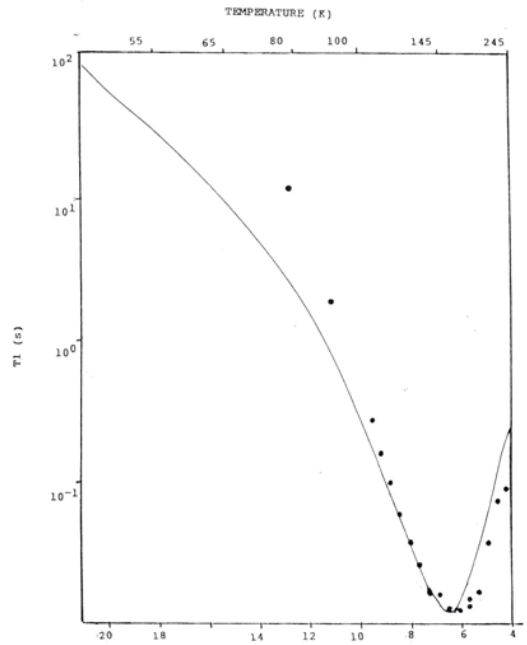


Fig. 3 The temperature dependence of T1 in Tert-methyl acetate at NMR frequency 21 MHz.

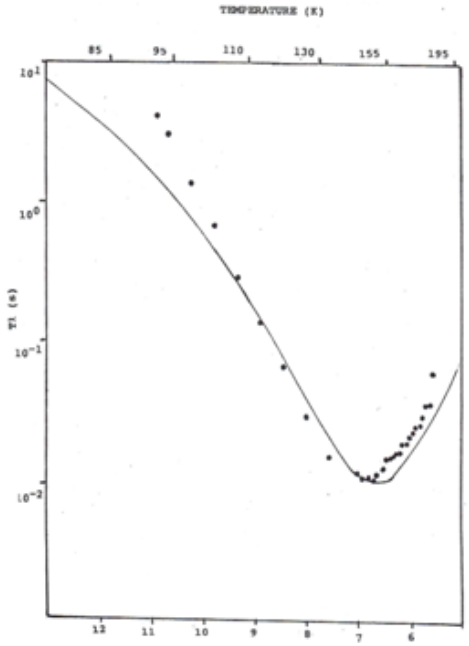


Fig. 4 The temperature dependence of T1 in tert-butyl -nitrite at NMR Frequency 21 MHz.

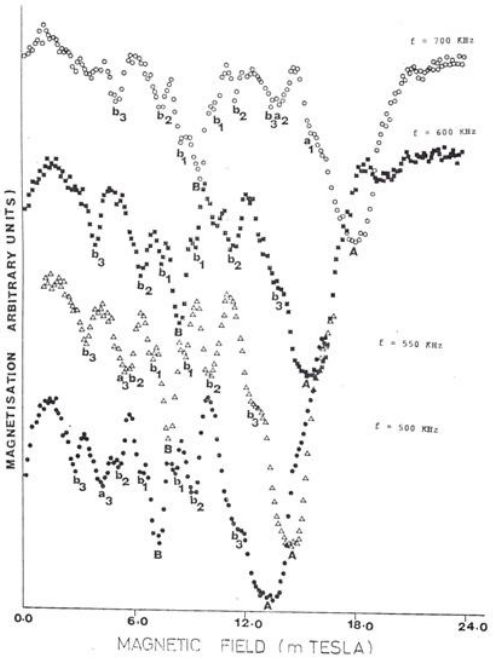


Fig. 5: The low field NMR spectra (4k) of Tert-Butyl hypoclorid recoded at a veriety of frequency. See text for details.

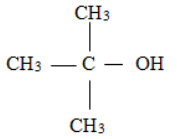
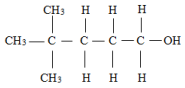
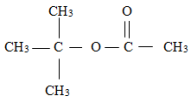
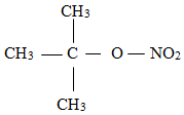
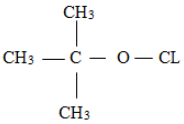
Sample	Structure Formula	T min [k]	vt Hz predicted	vt KHz measured	V3 [k]	E^a [k]
Tert-butyl alcohol		163	8×10^4	170±2 127±2	1850	770
2,2, Dimethylpent anol		74.7 148.8	0.6×10^7 0.5×10^5		1100 2050	577 1211
Tert-methyl acetate		114.3	1×10^6		1600	1240
Tert-Butyl nitrate		146.8	0.7×10^5		2000	1180
Tert-Butyl hypoclorid		165	8×10^4	382±5 112±5 90±5	1780	480

Table 1.