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ORIGINAL RESEARCH ARTICLE

Effect of temperature on tunneling frequency and dynamic behavior of methyl groups in some organic samples

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ABSTRACT

The Measurements of temperature relaxation (T_1) of methyl groups $(CH_3)_3$, the tunnel splitting (υt Hz), and energy activation (Eg) of some organic chemistry samples were done in this work. The Measurements were performed at different temperature ranged from 4 – 300 K. It was found that the Eg values for all the compounds ranged from 480-1240 kg/mol and the data was used to measure the magnitude values of the potential energy barriers (V_3) of the $(CH_3)_3$ in these compounds. The thermal composition mechanism was also investigated and the results indicate the relationship between the hopping rate and the form and height of the levels hindering barriers of collective motion of methyl group protons in samples. In this research, additional calculation for CH_3 tunneling splitting as a result to tunneling frequency was also performed.

Keywords: spin lattice; methyl group; tunnel splitting; dipole-dipole driven; nuclear magnetic resonance (NMR)

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1. Introduction

Recently, research into the properties of compounds containing methyl groups has increased significantly due to the intrinsic spin-lattice relaxation of protons which makes it possible to study methyl group $(CH_3)_3$ using nuclear magnetic resonance and neutron scattering techniques. The methyl group has a particular advantage which is the possibility of determining the barrier height independently of the hopping motion through observation of the tunnel process at minimum temperature. The choice of the NMR for the study of the behavior of methyl groups can be explained by its usage by many authors in the literature[1]. The Behavior of tunneling rotation rate of methyl groups, CH_3, is normally measured by using the rotation molecular reaction composition of the methyl group due to the hindering potential energy barriers of the rotation and the symmetry of $(CH_3)_3$; this potential barrier at least 3-fold symmetry[2]. The tunnel splitting of CH_3 is mostly done at low temperatures to ensure the symmetrical groups undergo a coherent oscillation and periodically penetrate the rotational barriers[3]. The initiation of the hindering potential indicate as a result to internal rotation of the methyl group is often assumed to be due electrostatic, Van der Waals and hard- core repulsive forces[4]. It is generally made up of intra-molecular interactions of methyl groups with the rest of the molecules

to which it is attached, and inter-molecular interactions with the non-bonded atoms in the sample.

The rotational Hamiltonian for a hindered group is given as:

$$H_R = (-\hbar^2/2I)\frac{d^2}{d^2\phi} + V_{3/2}\,[1\text{-}Cos(3\phi)] \quad (1)$$

Where $V_{3/2}$ is the potential energy which must have three-fold symmetry in ϕ due to the indistinguishability of the three methyl[5].

Furthermore, the motion behavior of CH_3 can be studied and explained by the excitation and relaxation processes within the energy levels ladder. In addition to that dynamics behavior is interpreted theoretically using the photon interaction expression which confirms a thermal distribution and enables the determination and maintenance of the Boltzman of the energy levels ladders[6,7]. Another theoretical approach[8] has also been used, as well as the principle of quantum mechanics which has been formalized to determine special parameters; The theory contains the hindering potential rotation of methyl groups in molecular solid as a term for barriers energy height[9]. In this work, the aim is to determine the behavior of $(CH_3)_3$ when its atoms are in contact with different atoms. the purpose of this study to focus the relation between temperatures and spin-lattice relaxation time (T_1) for all methyl groups and to add another test the validity of the model proposed by Clough et, al. The selected materials have methyl groups and the NMR technique was used as an ideal tool for the studying of rotational state tunneling and tunnel splitting of some molecules containing methyl groups, such as CH_3[10].

2. Experiments

2.1. Methods

During this work, NMR tool was used to achieve the experimental measurements as described by[11,12]. Two kinds of NMR experiment were performed; **(a)** dipole-dipole driven NMR technique which was used to calculate the tunneling splitting of CH3 methyl group[13]; (**b)** Measurements of the spin- lattice relaxation time (T_1) which was achieved using the NMR technique to show the dynamic behavior of methyl group (CH_3) in select Tert-butyl series and to perform the experimental measurement.

2.2. Materials

All the tertiary butyl compounds used in this work were supplied by Fulka Chemical company, U.K. the studied compounds were liquid at room temperature and prepared by using a freeze-pump thaw cycle[14]. To eliminate paramagnetic oxygen degassing under vacuum, a small volume of distilled sample was transferred into a sealed glass sample tube under a vacuum (10^{-5} Torr). The new work is devoted to the study of the dynamical behavior of methyl group in some materials chosen for this purpose such as (2,2 Dimethyl pentanol sample, Tert-butyl nitrite, Tert-methyl acetate specimen, Tert-butyl peroxide, and the pivalic acid sample).

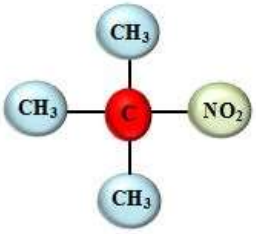
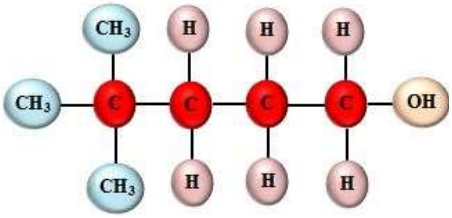
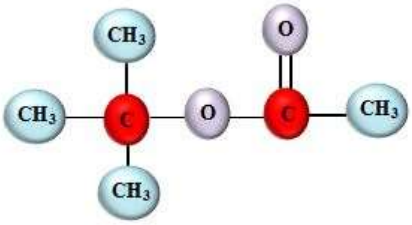
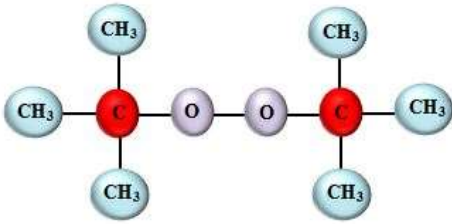
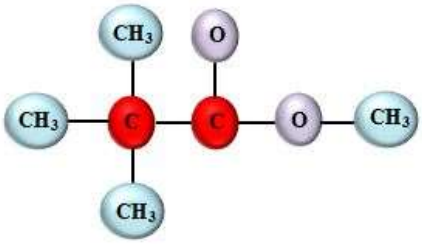
2.3. Characterization

NMR pulse spectrometry technique[15] which operates at 21 MHz was used for the measurement of the CH_3 tunnel splitting (υt KHz), proton spin lattice relaxation (T_1), barrier height (v_3 k), and activation energy (E_g (K)). In this work, barrier height and activation energy depend on temperature variation because Tert-buty groups rotate as a whole at low temperatures. This study aid new ideas to explanation the nature and mechanism of the molecular reorientation behavior.

This is the first time a new bath formulation has been used to describe the tunneling motion and other characteristics of Tur-butyl. The value of the tunneling frequency, activation energy, and barrier height for the different samples are shown in **Table 1**. The splitting calculation shows that the value of tunnel splitting

depends on the barrier height, V_3, and tends towards Zero as the hindering is increased. At a low barrier, on the other hand, it tends towards $\hbar^2/2I$ where (I) represent the moment of the inertia of the methyl group (CH_3). The investigation in this work focused on samples with a potential barrier value of V < 2000k. In these investigations, the tunneling splitting was measured in the ground region because the tunneling can be observed only at low temperature.

Table 1. The values of the tunnel frequency and barrier height of compounds.

Samples	Compounds Structure Formula	T_1 min [K]	υt Hz predicted	υt KHz Measured	V_3 [K]	E^a [K]
Tert-butyl nitrite		146.8	0.7×10^5		2000	1180
2,2 Dimethyl pentanol		114.3	1×10^6		1600	1240
Tert-methyl acetate		74.7 148.8	0.6×10^7 0.5×10^5		1100 2050	577 1211
Tert-butyl peroxide		163	8×10^4	170±2 127±2	1850	770
Pivalic Acid		165	8×104	382±5 112±5 90±5	1780	480

3. Discussion and results

In some Tert-butyl specimen at the low values temperature minimum (T_1) occurs as a result to move weakly hindered methyl group $(CH_3)_3$. This behavior confirms that the Tert-butyl group as a whole is not

rotating as a result to the internal barrier rotation; the methyl rotation as a whole is not fast at this temperature where the spin-lattice relaxation time (T_1) minimum occurs. The tunneling frequency at low temperature was 0.7×10^5 Hz; this value is related to the three-fold barrier height value i.e 2000 K. The result of the measurement on the Tert-Butyl – nitrite is shown in **Figure (1)**, displaying that the lattice relaxation behavior of this simple (T_1) minimum is located at 148.8 K.

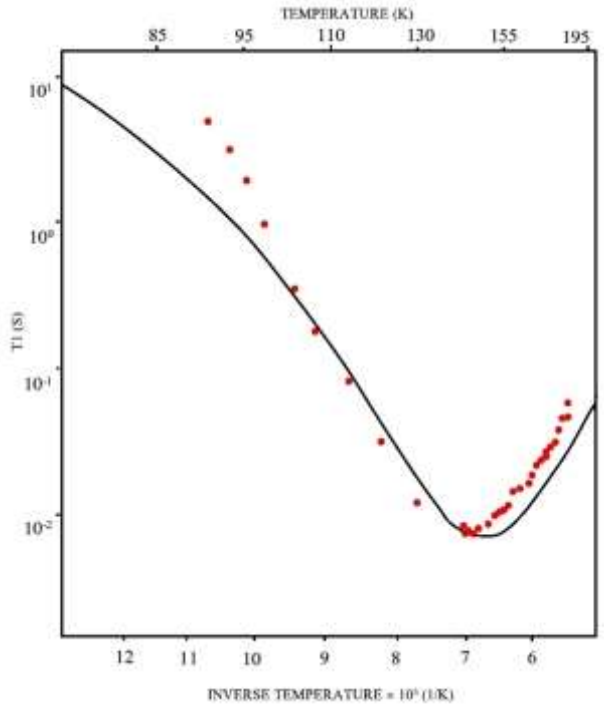


Figure 1. Temperature of T_1 minimum Tert-butyl nitrite sample at nuclear magnetic resonance frequency at 21 MHz.

Figure 2 shows the relaxation dynamic behavior of the Tert-methyl (CH_3) acetate where two minimums where observe in T_1 at 74.7 and 148 k. This sample has an interesting fact of relaxation behavior according to spin lattice relaxation which is dependent on the temperature. The value of the predicted barrier height (v_3) for $(CH_3)_3$ was 1100 K and the corresponding predicted tunneling splitting value for the first methyl group is 0.6×10^7 Hz, the value of tunnel splitting frequency for the second of the methyl group (CH_3) is 0.5×10^3 Hz. These values correspond measured to hindering barrier height value 2050 K.

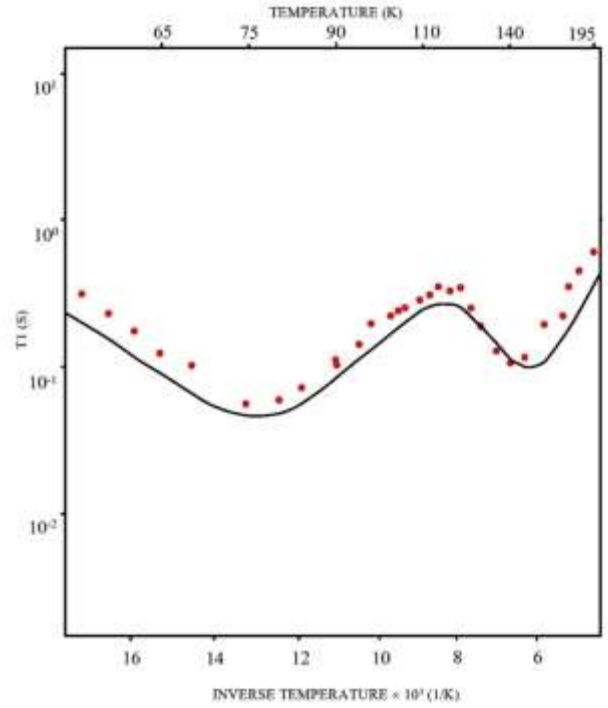


Figure 2. Temperature of T_1 dependent on temperature inverse for Tert-methyl acetate sample at frequency was (21 MHz).

Figure 3 shows the results for the (T_1) versus with temperature inverse for the peroxide sample; its T_1 minimum was obtained at 163 k. The predicted tunnel splitting is 1×10^6 Hz and the barriers height (v_3) is 1850 K.

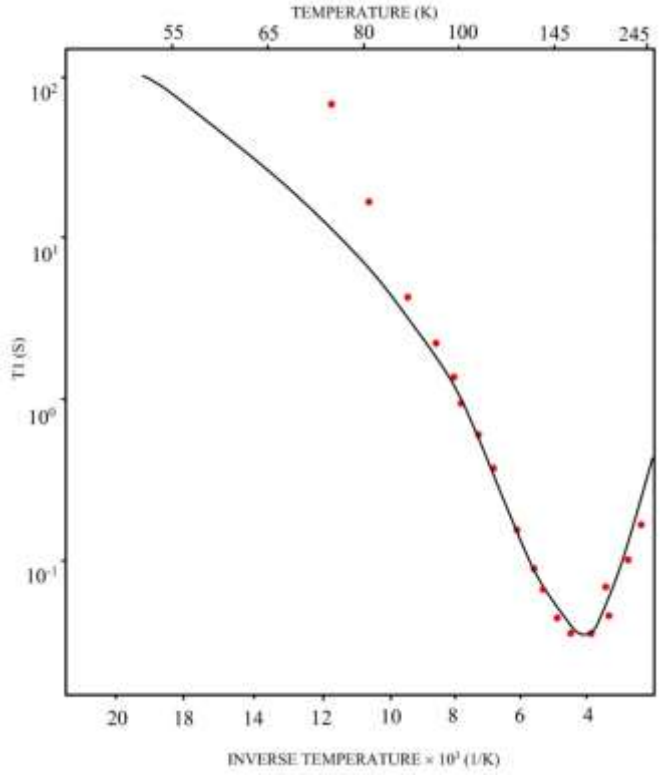


Figure 3. Temperature of T_1 minimum in Tert-butyl peroxide at (NMR) tunnel frequency was 21 MHz.

Figure 4 shows the relaxation behavior for 2,2 dimethyl propionic acid; in this sample, T_1 minimum was observed at 165 K while the predicated tunnel splitting was 8×10^4 and it the barrier height 1780 K.

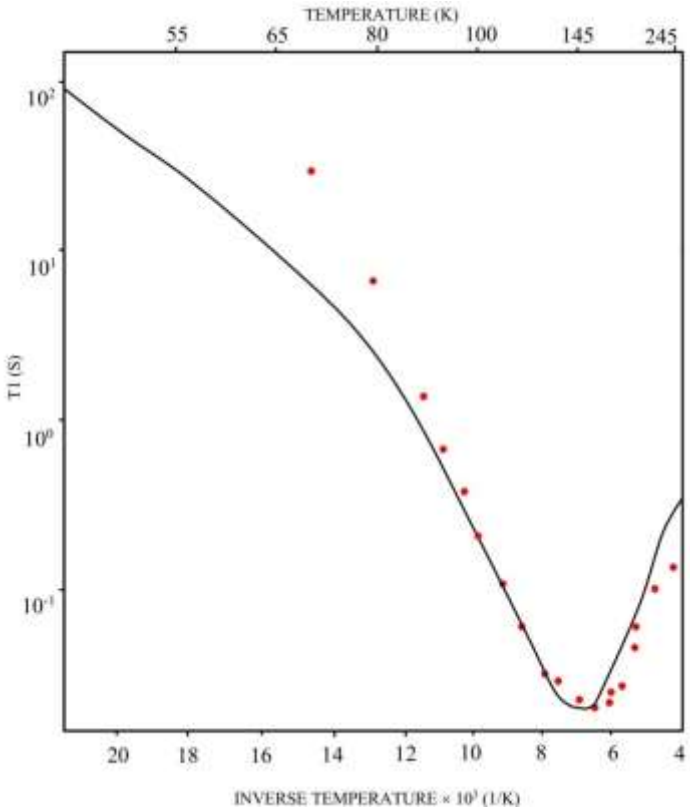


Figure 4. Temperature of T_1 minimum for (2,2 dimethyl propionic acid) when the (NMR) frequency was 21 MHz.

In the Figures above, the sold line represents the theoretical line deduced from[16], and it is used as a fit to the reorientation rate for the methyl group. The thermometer model was used to calculate the three-fold barrier height (v_3) and the experimental data agreed well with the calculated values.

Figure 5 shows the update correlation cure for the tunnel frequency as a function of temperature depends, when (T_1) becomes minimum observed for different compounds, including the four compounds mentioned above. Thus, the calculated data was for the spin-lattice relaxation in some material solids at different temperatures. All these measurements confirmed the correlation between tunnel splitting and temperature. We attribute (T_1) minimum as a result to the internal barrier of methyl groups (CH_3) in molecular environment.

Another important point to note is that the motion of methyl groups is fairly strong and hindered at a height temperature (T_1) minimum. The tunnel splitting obviously plays a key role in the height temperature; the classical BBP theory[17], measures the proper value at height temperatures; this theory has also been modified by[18] to involve extra compounds to account for the spectral density as a function of the tunneling of methyl group.

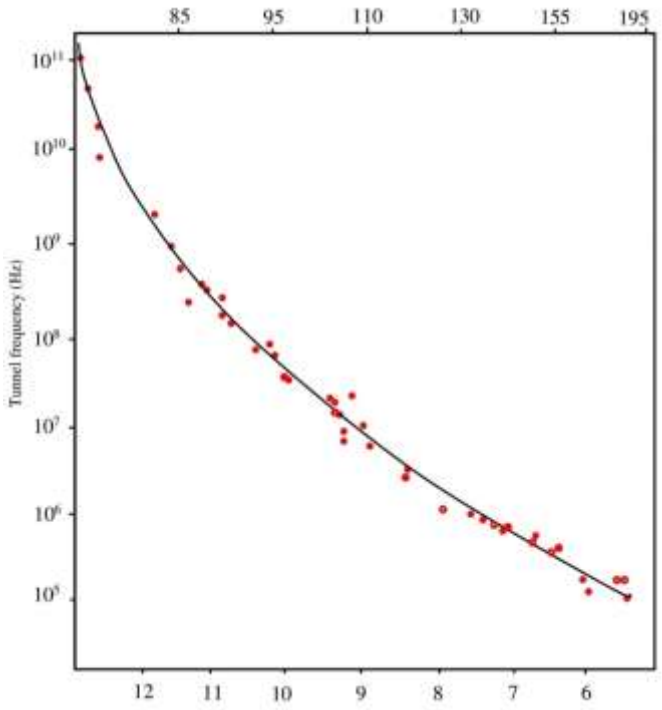


Figure 5. Shows Clough Correlation between the tunnel frequency with versus temperature when T_1 is a minimum observed for the methyl group sample, the seven open circles represent new data for some samples.

The nuclear magnetic resonance technique has been used in this work to measure the values of the tunnel splitting at 4 K and the barrier height for 2,2 dimethyl acid and tret-butyl peroxide. The values of the tunnel frequency and barrier height of these compounds are shown in Table 1. The results obtained for pivalic acid at different irradiations and different frequencies, such as (500 MHz, t= 20 s), (550 MHz, t= 20 s), (600 MHz, t= 20 s), (700 MHz, t= 20 s), (800 MHz, t= 20 s) and (850 MHz, t= 20 s) are shown in **Figure (6 a, b)**. All spectra show a clear position for

$\Delta m = 1$; the transition lies at approximately 14 mT. This displacement is observed at field values given as

$$B = \frac{\omega}{2\pi} \tag{2}$$

where (ω) represent the Larmar frequency and its value is 21 MHz[19]. With a sideband at lower field frequency, the second sideband $\Delta m = 2$ spectrum can be seen at ~ 8 mT; their tunnel frequencies lie at (282 ± 5), (112 ± 5) and (90 ± 5) KHz.

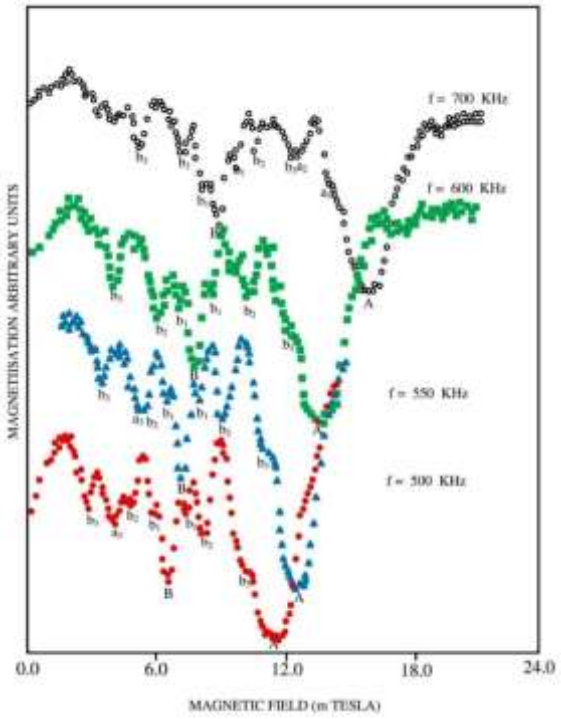


Figure 6-a. The low field nuclear magnetic resonance (NMR) spectra (4 K) of pivalic acid specimen measured at a variety of the frequency.

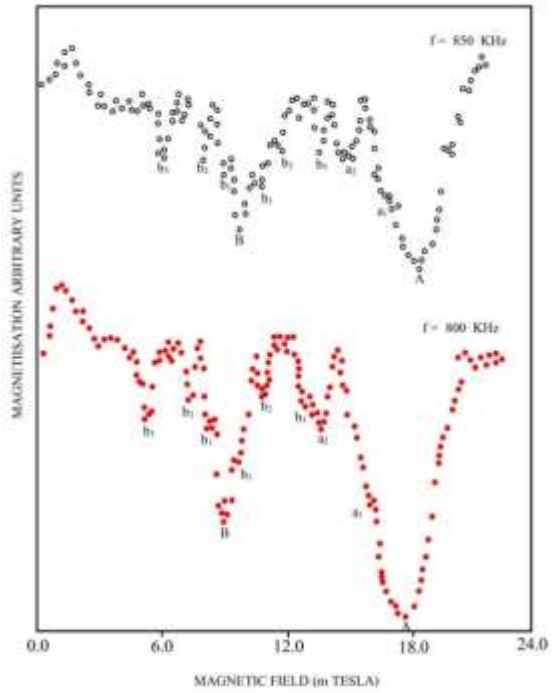


Figure 6-b. The low field nuclear magnetic resonance (NMR) spectra (4 K) of pivalic acid specimen measured at a variety of the frequency.

Note that the main height field moves increases in the irradiation frequency, but the sideband transition position remains constant. At these frequencies, the upper sideband is change as noted by S. Clought *et. al* 1981. Though, all these features are related to the shape of the level crossing of energy level graph occurring at 8 m_T[20]. The spectra data for Tert-butyl peroxide and pivalic acid are similar; **Figure 7** shows the results for an irradiation frequency of 500 KHz at different times. A filed cycling routine was used to observe the behavior of the spin relaxation for protons in level-crossing region[21]. Two sidebands ($\Delta m = 1$ and $\Delta m = 2$)

transition can be easily observed, al well as two minimum tunnel frequencies located at (170 ± 2 KHz, t= 30s) and (127 ± 2 KHz, t= 30 s). **Figure 8** shows the relation between T_1 versus as differences temperature for Tert-butyl peroxide samples, similar shoulder are seen in Δm = 1 peak at other difference irradiation frequencies (υt). These are very intensity in the same way to those seen in pavalic acid.

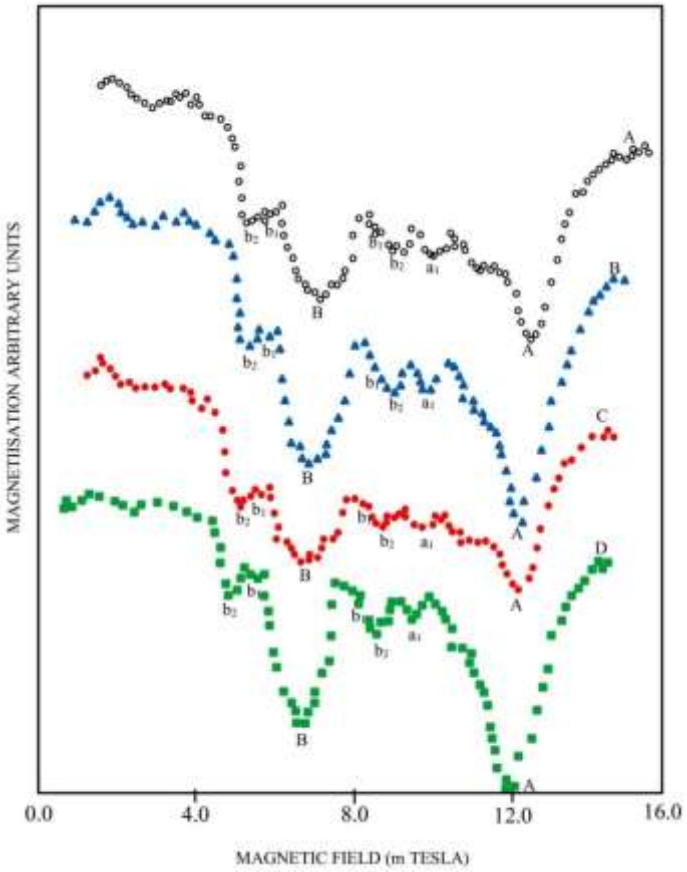


Figure 7. shows the low field nuclear magnetic resonance spectra at temperature (4 K) for Tert-butyl peroxide by using radio frequency RF= 500 KHz at difference time Where: (A.t=30s, B. t=20s, C. t=40s and D. t=12s) respectively.

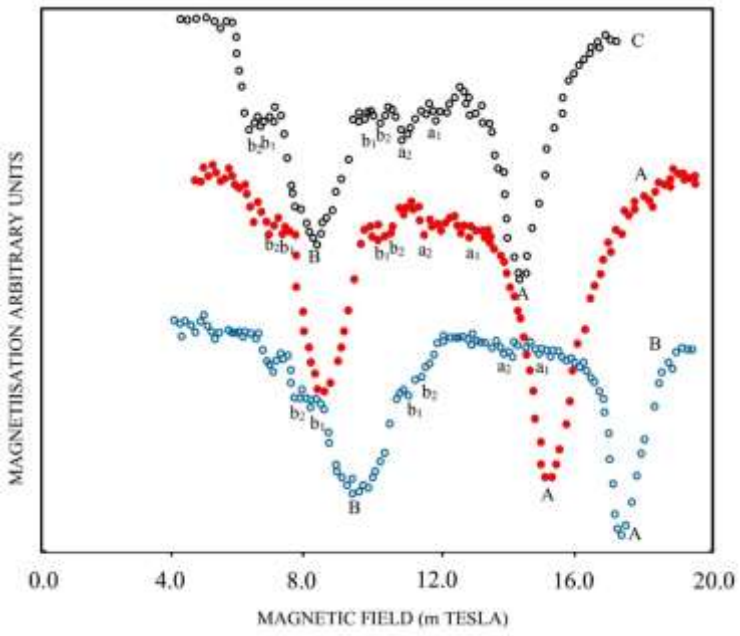


Figure 8. shows the low field nuclear magnetic resonance spectra at temperature (4 K) for Tert-butyl peroxide at difference value (A. RF= 500 KHz, B. RF= 600 KHz, and C. RF= 700 KHz) respectively.

4. Conclusion

The relaxation temperature relaxation of $(CH_3)_3$ and tunnel splitting of some Tert-butyl compounds has been extensively studied to investigate the systematics of these materials. An automated NMR technique was considered suitable for this study as it provided a wide range for measuring both energy activation and potential barriers (V_3). The result of the methyl group are in general agreement with those of Clough et.al. These compounds produced reasonable values for the tunneling splitting. Tert-butyl groups were chosen for investigation because they offer an opportunity to study the effects of the internal hindering barrier on the position of (T_1) minimum which shows at (~ 165 k) for some compounds. On another side, some of the samples exhibited low (T_1) below 165K and the only reason for this behavior is that the methyl groups have lower hindering and rotates as a whole $(CH_3)_3$. This study is considered an important steps toward more detailed investigation of the behavior of these materials at low temperature.

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Conflict of interest

The authors declare no conflict of interest.

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