Multiple pulse sequences are widely used for signal enhancement in NQR detection applications. Since the various $^{14}$N NQR relaxation times, signal decay times and frequency of each NQR line have a major influence on detection sequence performance, it is important to characterise these parameters and their temperature variation, as fully as possible. In this paper we discuss such measurements for a number of the $\nu_+$ and $\nu_-$ NQR lines of monoclinic and orthorhombic TNT and relate the temperature variation results to molecular dynamics. The temperature variation of the $^{14}$N spin-lattice relaxation times $T_1$ is interpreted as due to hindered rotation of the NO$_2$ group about the C–NO$_2$ bond with an activation energy of 89 kJ mol$^{-1}$ for the ortho and para groups of monoclinic TNT and 70 kJ mol$^{-1}$ for the para group of orthorhombic TNT.

Keywords: TNT detection, $^{14}$N NQR, NQR relaxation times, NQR parameters, temperature variation, pulsed spin-locking (PSL) sequence.

1. Introduction

Many nitrogen compounds, particularly those containing nitro groups, such as the explosive 2,4,6-trinitrotoluene (TNT) C$_6$H$_3$(NO$_2$)$_3$CH$_3$ (Fig. 1) have $^{14}$N nuclear quadrupole resonance (NQR) frequencies [1,2] below 1 MHz, where inductive methods of signal detection have poor sensitivity. In detection applications of NQR [3] various multiple pulse sequences are often used to improve sensitivity by rapidly regenerating signals. Optimisation of sensitivity is crucial and it is important to have full characterisation, including temperature variation, of the
various NQR parameters because of their influence on detection sequence performance. The main parameters are NQR line frequency, $T_1$ – the spin-lattice relaxation time, $T_2$ – the spin-spin relaxation time, $T_2^*$ – the signal decay time and $T_{2e}$ – the decay time of echo trains generated by multiple pulse sequences of the pulsed spin-locking (PSL) type [2 – 5]. This paper presents the results of such measurements for $\nu_+$ and $\nu_-^{14}$N NQR lines of monoclinic and orthorhombic TNT. The temperature variation of the NQR frequencies and their assignment to specific nitrogen sites are discussed and the temperature dependence of relaxation times related to the molecular dynamics.

![Fig. 1. The molecular structure of 2,4,6 trinitrotoluene (TNT). The carbon, hydrogen, oxygen and nitrogen atoms are coloured black, white, red and blue respectively. (For interpretation of colour mentioned in this figure the reader is referred to the on-line version of the article.)](image)

2. Experimental methods

TNT is known to exist in at least four different forms, two of which are monoclinic and two orthorhombic [6–12]. The common monoclinic [6,7] and orthorhombic [8] forms both have a crystallographic repeat unit which consists of two molecules, so both groups of $\nu_+$ and $\nu_-^{14}$N NQR transitions consist of six lines. The monoclinic TNT is the stable polymorph up to its melting point at 81°C although the metastable orthorhombic form can survive for long periods at ambient temperatures, but it converts to monoclinic near 70°C with a low enthalpy of transformation [7] and can convert slowly at intermediate temperatures. As an explosive TNT is stable to beyond its melting point. For the work here, we used a sample of monoclinic “creamed” TNT phase prepared by melting flakes of TNT which were then seeded with the finely-ground monoclinic form. The orthorhombic phase sample was prepared by fast quenching of the molten form on a cold surface at $-10 \, ^\circ$C. The two TNT samples were prepared, characterised and supplied to us by the Defence Science and Technology Laboratory, Fort Halstead, U.K.

The $^{14}$N NQR measurements presented here were conducted on a Tecmag “Libra” pulsed RF spectrometer. For the line frequency and relaxation time variable temperature work the NQR probe, which had a Q of around 90, consisted of an RF solenoid coil mounted in a screening can inserted into a glass
Dewar filled with silicone oil. A length of coaxial cable connected the coil to parallel tuning and series matching capacitors mounted in a die-cast aluminium box at the mouth of the Dewar. A platinum resistance temperature sensor clamped to the side of the coil screening can was used to monitor and control the temperature via a Eurotherm temperature controller. For low temperature measurements this controlled the solenoid valve of a refrigerated cold finger immersed in the silicone oil bath; the temperature control was to within ±0.5 °C. For high temperature measurements, an immersion heater was used as well as the cold finger so temperature control was better and was within about ±0.25 °C. The immersion heater was constructed from a small 240 V 350 W cartridge heater (RS 837-666) soldered concentrically to the end of a length of stainless steel tube through which the connecting wires passed to the temperature controller. A capillary thermostat (RS 561-460) mounted on the stainless steel tube above the heater was wired in series with the heater to provide an over-temperature safety cut out should the temperature controller fail in such a way that the heater was full on, an important precaution when studying explosive materials. A length of copper sheet was fitted to the cartridge heater to provide better conduction through the oil bath. The temperature range selected (−30°C to +50°C) was regarded as appropriate for conditions likely to be encountered in mine clearance and other security operations. \( T_1 \) relaxation times were mostly measured using a steady state method which involved detecting the line concerned with different repeat times between RF pulses (or sequences of pulses) covering the range up to 5 or 6 times \( T_1 \). Plots of peak spectral line intensity versus repeat time gave \( T_1 \) recovery curves from which \( T_1 \) values were obtained from fits assuming single component exponential \( T_1 \) relaxation. To speed up signal collection at the lowest temperatures, pulsed spin-locking (PSL) \([2-5]\) echo summation sequences were used to enhance the TNT signals. Shorter \( T_1 \) values at high temperature, were measured using the inversion recovery method and for some temperatures and NQR lines the \( T_1 \) measurements were repeated with both methods and the results were found to be in reasonable agreement. Good fits to the \( T_1 \) recovery curves were obtained with a single exponential term. \( T_{2e} \) was measured using a PSL sequence, each sequential data block of a full PSL sequential echo signal train was Fourier transformed and the peak real spectral line intensity of each block used to plot decay curves from which \( T_{2e} \) was obtained using the exponential fit \( A_0 e^{-2\pi T_{2e}} \).

3. Results and discussion

3.1. Temperature variation of TNT \(^{14}\)N NQR frequencies

The \(^{14}\)N NQR \( \nu_+ \) and \( \nu_- \) line frequencies as a function of temperature have already been published for both the monoclinic and orthorhombic form of TNT \([1,2,3,13,14]\). Over the temperature range −30°C to +50°C (243 K to 323 K) used for our measurements here the variation of line frequency with temperature is close to linear. There is no evidence for any large-amplitude whole-molecule
motion nor interconversion between the two non-equivalent molecules in each form of TNT. A major contribution to this temperature dependence is expected to come from those librational modes involving torsional oscillation of the NO$_2$ group, which at constant volume should follow the Bayer-Kushida equation [15]

\[
v(T) = v(0) - \frac{3h}{2} \sum_i \frac{A_i}{\omega_i} \left( \frac{1}{\exp(h\omega_i/kT) - 1} \right)
\]

where the zero temperature term $v(0)$ is given by:

\[
v(0) = v_0 \left[ 1 - \frac{3}{4} h \sum_i A_i / \omega_i \right]
\]

$\omega_i$ is the librational oscillation frequency of the $i$th mode, $v(T)$ is the NQR line frequency at a temperature $T$, and $v_0$ the resonance frequency in a fictitious "static" lattice. $A_i$ consists of two terms. The first is due to the averaging of the electric field gradient at the nuclear site by the torsional oscillations of the NO$_2$ group, for which $A_i = 1/I_i$ ($I_i$ being the corresponding moment of inertia), and the second is due to molecular distortion. The temperature variation of the NQR line frequencies in the 243 to 323 K linear region can be described by Eq. (2), a linear form of Eq. (1) obtained by taking the first 2 elements of the Taylor series for the exponential term and assuming one torsional mode $\omega_t$, viz. that about the C– NO$_2$ bond, to be the main contributor.

\[
v(T) = v(0) - \frac{3v_0}{2I_t (\omega_t)^2} kT = v(0) - bT
\]

The values of $v(0)$ and the temperature coefficient $b$ for all the $v_+$ and $v_-$ lines of both polymorphic forms obtained from linear fits to our line frequency measurements in the 243 – 323 K temperature range are given in Table 1. Table 1 also shows the twist angle of the plane of the nitro groups with respect to that of the benzene ring and the site assignments [14] to the two ortho (oA and oB) and para (p) nitro groups of the two molecules (I and II) of the crystallographic repeat unit. In both polymorphs, the lowest value of $b$ and the twist angle are found for the two para nitro groups which from Eq. (2) should therefore have the higher torsional frequencies. We assume $I_t$ to be 64.6 x 10$^{-47}$ kg m$^2$ for a nitro group [16] and approximate $v_0$ as 875 kHz which is the mean value of the 6 $v_+$ frequencies at 77 K [1] where the temperature variation is levelling off. The mean torsional frequency of the para groups is then calculated to be 91 cm$^{-1}$ and that for the ortho groups should cover a range from approximately 60 to 90 cm$^{-1}$. Similar values have been observed in other aromatic nitro compounds [17-21]. Also the terahertz spectrum of TNT [22,23] shows a number of features, broad peaks or inflections, from 60 to 100 cm$^{-1}$. A theoretical analysis [24] suggests that these features are “cog-wheel” torsional modes involving the 2,6 NO$_2$ groups with
the adjacent methyl group and predicts frequencies close to 70 and 91 cm\(^{-1}\) for the two molecules (I and II) of the crystallographic repeat unit.

**Table 1**

\(\text{\(^{14}\text{N NQR } \nu_+\text{ and } \nu_-\text{ line frequencies for monoclinic and orthorhombic TNT have previously been published over a range of temperatures [1,2,3,13,14]. This table presents the linear fit parameters, } \nu(0)\text{ and temperature coefficients } b\text{, of Eq. 2 for the } \nu_+\text{ and } \nu_-\text{ NQR lines of both polymorphs of TNT, obtained from our line frequency measurements in the 243 – 323 K temperature range. As elsewhere in this paper NQR lines are identified by their frequency at 22 °C (295 K). The NO}_2\text{ site assignments for each line are shown along with the twist angle of the plane of the NO}_2\text{ groups obtained from the crystallographic data [6]. The labels I and II distinguish each molecule of the pairs in a unit cell, A and B label different ortho nitro groups.}}\)**

<table>
<thead>
<tr>
<th>Site</th>
<th>Monoclinic TNT</th>
<th>Orthorhombic TNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu_+) [kHz]</td>
<td>(\nu_-) [kHz]</td>
</tr>
<tr>
<td>oA-I</td>
<td>859.2</td>
<td>921.18</td>
</tr>
<tr>
<td>oA-II</td>
<td>842.8</td>
<td>892.50</td>
</tr>
<tr>
<td>oB-I</td>
<td>848.3</td>
<td>893.50</td>
</tr>
<tr>
<td>oB-II</td>
<td>837.1</td>
<td>870.29</td>
</tr>
<tr>
<td>p-I</td>
<td>844.2</td>
<td>875.73</td>
</tr>
<tr>
<td>p-II</td>
<td>870.3</td>
<td>900.66</td>
</tr>
</tbody>
</table>

Marino et al. [1,2] measured the \(^{14}\text{N NQR } \nu_+\text{ and } \nu_-\text{ line frequencies for monoclinic TNT from 77 K to 321 K and for orthorhombic TNT from 77 K to 280 K. The line frequency variation with temperature is non-linear over these wide ranges with the rate of change decreasing to low temperature so reported temperature coefficients will vary somewhat depending on the temperature range selected for a linear fit. We compared the reported line frequencies [2] of both forms of TNT in the 243 to 323K temperature range by including them in plots of our data with the linear fits from this work and found good agreement between the two sets of measurements. The temperature coefficients of each NQR line of monoclinic TNT calculated from the data of Marino et al. are also tabulated in reference [3] and these values are shown in Table 2 along with our \(b\) values from Table 1 for comparison. There is good overall agreement between the two sets of values of \(b\) for monoclinic TNT with a mean difference of about 6% and largest difference of 12%, for the 844 kHz line. Table 2 also compares our \(b\) values for orthorhombic TNT with previously published values [36] and the overall agreement is good with a mean difference of about 8%, however here the largest difference is higher at 22%, for the 837 kHz line.
Table 2
The temperature coefficients $b$ (Eq. 2) and the $T_1$ values measured here compared to previously reported values for the $\nu_+$ and $\nu_-$ NQR lines of both polymorphs of TNT. For monoclinic TNT the $T_1$ values are for 22 °C from the work here and room temperature from Ref. [3]. For orthorhombic TNT the $T_1$ values are for 20 °C from the work here and 23 °C from Ref. [36].

<table>
<thead>
<tr>
<th>Line [kHz]</th>
<th>$b$ [Hz K$^{-1}$]</th>
<th>$T_1$ [s]</th>
<th>Line [kHz]</th>
<th>$b$ [Hz K$^{-1}$]</th>
<th>$T_1$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Here</td>
<td>Ref.[3]</td>
<td>Here</td>
<td>Ref.[3]</td>
<td>Here</td>
</tr>
<tr>
<td>870.3</td>
<td>103.0</td>
<td>109</td>
<td>3.0</td>
<td>4.0</td>
<td>868.3</td>
</tr>
<tr>
<td>859.2</td>
<td>210.2</td>
<td>223</td>
<td>12.0</td>
<td>3.0</td>
<td>860.9</td>
</tr>
<tr>
<td>848.3</td>
<td>152.9</td>
<td>151</td>
<td>13.0</td>
<td>9.6</td>
<td>848.1</td>
</tr>
<tr>
<td>844.2</td>
<td>107.0</td>
<td>121</td>
<td>6.5</td>
<td>4.7</td>
<td>846.5</td>
</tr>
<tr>
<td>842.8</td>
<td>168.5</td>
<td>181</td>
<td>4.5</td>
<td>3.5</td>
<td>841.7</td>
</tr>
<tr>
<td>837.1</td>
<td>112.5</td>
<td>122</td>
<td>4.3</td>
<td>2.1</td>
<td>837.1</td>
</tr>
<tr>
<td>768.7</td>
<td>178.7</td>
<td>190</td>
<td>16.0</td>
<td>9.8</td>
<td>768.9</td>
</tr>
<tr>
<td>751.1</td>
<td>233.4</td>
<td>241</td>
<td>3.0</td>
<td>2.2</td>
<td>752.1</td>
</tr>
<tr>
<td>742.9</td>
<td>135.2</td>
<td>148</td>
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<td>3.0</td>
<td>741.3</td>
</tr>
<tr>
<td>739.6</td>
<td>159.0</td>
<td>169</td>
<td>9.0</td>
<td>5.5</td>
<td>741.3</td>
</tr>
<tr>
<td>714.4</td>
<td>87.9</td>
<td>94</td>
<td>4.0</td>
<td>4.3</td>
<td>716.6</td>
</tr>
<tr>
<td>713.9</td>
<td>92.4</td>
<td>94</td>
<td>10.0</td>
<td>4.3</td>
<td>712.5</td>
</tr>
</tbody>
</table>

For TNT detection applications, since sensitivity increases with frequency, the obvious choice is to work with the $\nu_+$ NQR lines and usually the highest frequency lines at 870 kHz for monoclinic TNT and 868 kHz for orthorhombic TNT. Importantly these lines, which are both associated with the para-nitro groups, also have the lowest temperature coefficients making them the best choice for detecting this explosive when the temperature of the sample is uncertain. When the sample temperature is known and multiple resolved lines are detected, it is possible to use a “finger print” of line frequencies (usually the four lines from 848 to 837 kHz), to enhance the signal-to-noise ratio (SNR) using approximate maximum likelihood parametric data processing [25].

3.2. The $^{14}$N NQR relaxation times and signal decay times of TNT

We have measured the $^{14}$N NQR spin-lattice relaxation time $T_1$ for all 12 $\nu_+$ and $\nu_-$ lines of both TNT polymorphs at various temperatures in the range 243 – 323 K and we have measured the temperature dependence of $T_1$ for some lines. The $T_1$ values obtained here for monoclinic TNT at 22°C (295 K) and orthorhombic TNT at 20°C (293 K) are presented in Table 2 where they are compared to the previously published values for orthorhombic TNT [36] at 23°C and monoclinic TNT [3] presumably at room temperature. Our $T_1$ values for nineteen of the NQR lines in Table 2 are in reasonable agreement with the previously reported values but four of our $T_1$ values are significantly different. For monoclinic TNT our $T_1$ values for the 859 kHz and 713.9 kHz lines are 12 s and 10 s respectively compared to the previously reported [3] values of 3 s and 4.3 s. For orthorhombic TNT our $T_1$ values for the 861 kHz and 848 kHz lines are 15 s and 17 s respectively compared to the published [36] values of 7.5 s and 5.5 s.
Fig. 2 presents results from our study of the temperature dependence of $T_1$ for a few of the $\nu_+$ lines of monoclinic and orthorhombic TNT selected to show both the variation of $T_1$ and in the spread of $T_1$ values with temperature. In detection applications the variation of $T_1$ with temperature can have significant impact on detection sensitivity or detection time.

![Fig. 2. The temperature variation of the $^{14}$N NQR spin-lattice relaxation time $T_1$ for a few of the $\nu_+$ lines of monoclinic and orthorhombic TNT.](image)

NQR spin-lattice relaxation times $T_1$ can be strongly influenced by slow molecular rotations and $T_1$ often becomes shorter to higher temperatures as such processes become more important, the temperature dependence of $T_1$ can then be used to gain some insight into such molecular dynamics [34,35,15]. Fig. 3 is an Arrhenius plot of our measurements of the temperature variation of the $^{14}$N NQR $T_1$ for the highest frequency $\nu_+ 870$ kHz and $\nu_- 769$ kHz lines of monoclinic TNT and the highest frequency $\nu_+ 868$ kHz line of orthorhombic TNT. The temperature variation falls into two regions with a step in the range $280 – 290$ K and Fig. 3 shows linear fits for each region using Eq. (3); the logarithmic form of the Arrhenius equation.

$$\ln(T_1) = \ln(A) + \frac{E_a}{R} \left( \frac{1}{T} \right)$$  \hspace{1cm} (3)
Fig. 3. Arrhenius plot of the temperature variation of the $^{14}$N NQR $T_1$ relaxation time for the $\nu_+ 870$ kHz and $\nu_- 769$ kHz lines of monoclinic TNT and the $\nu_+ 868$ kHz line of orthorhombic TNT. The line plots are linear fits using Eq. (3).

From the fits to the region of interest here, the higher temperature region above 280 – 290 K, we obtain an activation energy $E_a$ of 89 kJ mol$^{-1}$ for both the lines of monoclinic TNT while for the orthorhombic line we obtain the lower value of 70 kJ mol$^{-1}$ for $E_a$. In the lower temperature region the activation energies are 8.5, 0.6 and 13 kJ mol$^{-1}$ for the $\nu_+ 870$ kHz, $\nu_- 769$ kHz lines of monoclinic TNT and the $\nu_+ 868$ kHz line of orthorhombic TNT respectively.

The trains of echoes generated by multiple pulse sequences of the pulse spin-locking (PSL) type [2 – 5] decay with an effective relaxation time $T_{2e} > T_2$ which generally increases as the RF pulse spacing decreases. The echo trains are a mixture of Hahn (or direct) and stimulated echoes, with the latter introducing some $T_1$ dependence into the echo train decay time. $T_{2e}$ is not a fundamental relaxation time but depends on $T_1$, $T_2$, $T_{1p}$ ($T_1$ in the rotating frame) and $T_2^*$, so the dynamics of the $T_{2e}$ decay will be linked to that of these other relaxation times. Fig. 4 is an Arrhenius plot of our measurements of the temperature variation of $T_{2e}$ for the $\nu_+ 870$ kHz line of monoclinic TNT and the $\nu_+ 868$ kHz line of orthorhombic TNT. $T_{2e}$ was obtained from single exponential fits to echo trains obtained using PSL sequences, as described in section 2, with 2$\tau$ pulse spacings of 1.134 ms and 2.2 ms respectively for the monoclinic and orthorhombic TNT. Using the logarithmic form of the Arrhenius equation Eq. (3) for a linear fit to the three monoclinic data points as shown in Fig. 4 we obtain an $E_a$ of 71 kJ mol$^{-1}$ and similarly the linear fit to the eight highest temperature orthorhombic data points yields an $E_a$ of 78 kHz. We have not measured the spin-spin relaxation time $T_2$ over a range of temperatures but the values we have obtained at two temperatures for the $\nu_+ 870$ kHz line of monoclinic and the $\nu_+ 868$ kHz line of
orthorhombic TNT are also shown in Fig. 4 to illustrate the difference between $T_{2e}$ and $T_2$ and $T_1$ (Fig. 4). The two point linear fits for $T_2$ in Fig. 4 give an estimate of $E_a$ of 44 kJ mol$^{-1}$ for the 870 kHz line of monoclinic TNT and 31 kJ mol$^{-1}$ for the 868 kHz line of orthorhombic TNT.

![Fig. 4. Arrhenius plot of the temperature variation of the $^{14}$N NQR $T_{2e}$ echo train decay time and $T_2$ relaxation time for the $\nu + 870$ kHz line of monoclinic TNT and the $\nu + 868$ kHz line of orthorhombic TNT. The line plots are linear fits using Eq. (3).](image)

The high temperature activation energies are summarised in Table 3. The most likely explanation for the high temperature variation of $T_1$ and $T_{2e}$ is that they are both governed by the effects of hindered rotation of the NO$_2$ group about the C–NO$_2$ bond. This model may be supported by $^{17}$O double resonance NMR/NQR experiments which show that no $^{17}$O signals from the NO$_2$ groups could be detected above 230 K [26]. This may be due to a broadening of the lines caused by interchange of the oxygen atoms following rotation of the NO$_2$ group, which would produce a considerable change in the electric field tensor at the oxygen site. We have found from similar work on the temperature variation of $T_1$ in the explosive RDX [27] that $E_a$ is 92 kJ mol$^{-1}$ for hindered rotation about the N–NO$_2$ bond and for the explosive PETN [16] that $E_a$ is 24.5 kJ mol$^{-1}$ for rotation about the O–NO$_2$ bond. In the isolated TNT molecule the energy barrier for nitro group rotation is calculated to be 10.6 kJ mol$^{-1}$ [24], indicating that solid state interactions must make a major contribution to our measured values. For C–NO$_2$ groups in other molecules, where this behaviour is expected to be a common feature [28,29], the literature values for rotational activation energies vary considerably. For example they are estimated to be larger than 31 kJ mol$^{-1}$ in m-chloronitrobenzene [17], 22.7 kJ mol$^{-1}$ for the para and 35.4 kJ mol$^{-1}$ for the ortho NO$_2$ groups in 2,4-dinitrochlorobenzene [18], close to 12 kJ mol$^{-1}$ in 3– and 4–nitrobenzene sulphonyl chlorides but 29 kJ mol$^{-1}$ for the 2–form [19], 27.4 and
31.2 kJ mol\(^{-1}\) for the two ortho groups in 2,4,6-trinitrochlorobenzene (picryl chloride) [20] and 17.5 kJ mol\(^{-1}\) in 1-chloro-2,4-dinitrobenzene but a mean value of 13.6 kJ mol\(^{-1}\) in 1,2-dichloro-3-nitrobenzene [21]. In gaseous nitrobenzene, a planar molecule, values of 12 ± 6 [30] and 17 ± 4 kJ mol\(^{-1}\) [31] have been measured. These values seem to bear little relationship to the C–N bond length; its average values in the two molecules in the monoclinic form of TNT are 147.5 pm [6] and 148.2 pm [8], in the orthorhombic form the average of the two is 147 pm and in gaseous nitrobenzene 146.8 pm [31]. Our values of \(E_a(T_1)\) in Table 3 suggest there is little difference between the ortho and para NO\(_2\) groups in monoclinic TNT since for both the activation energies are close to 90 kJ mol\(^{-1}\) but for orthorhombic TNT, at least for the para group, \(E_a(T_1)\) is somewhat lower at 70 kJ mol\(^{-1}\). However, comparisons between these \(E_a\) values may not be very meaningful in view of the likely variations in the shape of the potential energy curves. In the case of TNT, one reason for the variations listed in Table 3 may lie in differences in the twist angles given in Table 1; the para NO\(_2\) groups may need to rotate by only 44° to reach an almost equivalent energy position, whereas this angle would need to lie between 92° and 120° for the ortho NO\(_2\) groups.

**Table 3**
The high temperature activation energies \(E_a\) for \(T_1\), \(T_2\), and \(T_2\) of the \(\nu\), 870 kHz and \(\nu\), 769 kHz lines of monoclinic TNT and the \(\nu\), 868 kHz line of orthorhombic TNT obtained from the fits using Eq. (3) in Figs. 3 & 4 as discussed in the text.

<table>
<thead>
<tr>
<th>Site</th>
<th>Line [kHz]</th>
<th>Monoclinic TNT</th>
<th>Orthorhombic TNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_a) [kJ mol(^{-1})]</td>
<td>(E_a(T_1))</td>
<td>(E_a(T_2))</td>
</tr>
<tr>
<td>p-II</td>
<td>(\nu), 870</td>
<td>89</td>
<td>71</td>
</tr>
<tr>
<td>oA-II</td>
<td>(\nu), 769</td>
<td>89</td>
<td>—</td>
</tr>
</tbody>
</table>

We have examined the \(\nu\), 870 kHz spectral line of monoclinic TNT at various temperatures and found the line shape to be a good fit to a Lorentzian profile for which the full width at half height \(\Delta\nu_{1/2}\) is related to the signal decay time \(T_2^*\) via \(\Delta\nu_{1/2} = 1/(\pi T_2^*)\). Lorentzian line shapes are expected when the dominant term is damping of the Larmor precession of the magnetization in the electric field gradient due to relaxation [32]. The temperature variation of \(\Delta\nu_{1/2}\) is shown in Fig. 5 together with a plot of the natural width \(\Delta\nu_{1/2} = 1/(\pi T_2)\) obtained from the parameters of the fit to \(T_2\) in Fig. 4.
Fig. 5. The temperature variation of full width at half height $\Delta \nu_{1/2}$ for the $\nu + 870$ kHz $^{14}$N NQR line of monoclinic TNT and a plot of the natural width $\Delta \nu_{1/2} = 1/(\pi T_2)$ obtained from the parameters of the fit to $T_2$ in Fig. 4.

Recognising that the observed line shape function is a convolution of inhomogeneous broadening and the natural line shape function and assuming both to be Lorentzian we can write [27]:-

\[
\frac{1}{T_2^*} = \frac{1}{T_2(\text{inhom})} + \frac{1}{T_2}
\]

where $T_{2(\text{inhom})}$ is the inhomogeneous decay time. Since $T_2$ increases to lower temperature $1/T_2$ rapidly becomes negligible and we have $(1/T_{2(\text{inhom})})_{T=0} = (1/T_2^*)_{T=0}$. Fig. 6 shows the temperature dependence of $1/T_{2(\text{inhom})}$ calculated via Eq. (4) and the data in Fig.5. From the linear fit, which represents the temperature dependence of $1/T_{2(\text{inhom})}$ as

\[
1/T_{2(\text{inhom})}(T) = \left[ (1/T_{2(\text{inhom})})_{T=0} + \alpha T \right] \text{ or } \left[ (1/T_2^*)_{T=0} + \alpha T \right]
\]

we obtain $\alpha$, the temperature coefficient of $1/T_{2(\text{inhom})}$, as -0.018 ms$^{-1}$K$^{-1}$. This has the same sign but is a factor of four larger than value of $\alpha$ observed for RDX [27] where it was attributed to changes in the torsional frequency of the NO$_2$ groups at dislocations. This may also be the case for TNT since the major defects in TNT crystals are growth-induced defects such as growth sectors and boundaries, solvent inclusions, edge or screw dislocations and stacking faults [33]. The parameter $\alpha$ may of course be sample dependent and could provide some information on sample origin.
Fig. 6. The temperature variation of $1/T_{2\text{inhom}}$ for the $\nu_+ 870$ kHz $^{14}$N NQR line of monoclinic TNT. The line plot is a linear fit using Eq. 5.

4. Conclusions

We have measured the various $^{14}$N NQR parameters for a number of the $\nu_+$ and $\nu_-$ lines of monoclinic and orthorhombic TNT over a range of temperatures and discussed the temperature variation of some of these parameters in terms of the molecular dynamics. The temperature dependence of $T_1$ has been explained as due to hindered rotation of the NO$_2$ group about the C–NO$_2$ bond with an activation energy of 89 kJ mol$^{-1}$ for the ortho and para groups of monoclinic TNT and 70 kJ mol$^{-1}$ for the para group of orthorhombic TNT.

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References


