# Complete Computer Analysis of NQR Data

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Theories explaining temperature dependences of frequency, line width and spin-lattice relaxation times in Nuclear Quadrupole Resonance (NQR) spectroscopy have been presented in the form of mathematical expressions. Hence a complete analysis of experimental data can easily be implemented on any microcomputer. This was demonstrated by the results obtained from $^{35}$Cl NQR studies of *p,p'*-DDT. The computer analysis allowed to separate different mechanisms of quadrupole relaxation and determine characteristic parameters: moments of inertia of the molecule, librational frequencies and activation energies of rotating molecular groups. Besides numerical values, the printer working with the computer can produce plots of experimental points in different coordinate systems as well as the fit curves.

The parameters most frequently studied in NQR spectroscopy are the resonance frequency ($\nu_Q$), line width ($\delta\nu_Q$), and spin-lattice relaxation time ($T_1$). Temperature studies of these parameters allow for determination of molecular dynamics in solids, mainly librations and hindered rotations of atomic groups. There are many theories relating individual spectroscopic parameters to molecules and their dynamics. All these theories can be expressed as more or less complex mathematical formulas. The accurate fit of experimental results to these expressions allows for a direct determination of physical parameters of interest. The aim of this paper is to show that the complete numerical and graphical analysis of NQR data can successfully be achieved on any accessible microcomputer.

## Temperature Dependences of Basic Parameters in NQR Spectroscopy

Let us consider the influence of molecular motions on individual parameters of NQR spectrum studied as a function of temperature. As is known from infrared studies, the librational frequencies in molecular crystals range from $10^{11}$ Hz to $10^{13}$ Hz, so they exceed considerably the NQR frequencies of $10^6$—$10^8$ Hz. Therefore the librational motions cause only an averaging of electric field gradient seen by the resonant nuclei. Bayer[1] assumed that NQR frequency decreases with increasing temperature only due to an increase in the amplitude of librational motions. He treated a molecule as a quantum harmonic oscillator and obtained the following expression for a temperature dependence of NQR frequency:

$$\nu_Q(T) = a - \frac{b}{\exp(c/T) - 1}, \tag{1}$$

$$a = \nu_Q(0), \tag{2}$$

$$b = \frac{6\hbar\nu_Q(0)}{4I\omega_l - 3\hbar}, \tag{3}$$

$$c = \frac{\hbar\omega_l}{k}. \tag{4}$$

$\nu_Q(0)$ is the NQR frequency at 0 K, $I$ is the relevant moment of inertia, $\omega_l$ is the librational frequency of the molecule. However, experiments have yielded only qualitative agreement with Bayer's theory. Better agreement with the theory could have been obtained if other types of molecular vibrations as well as thermal expansion had been taken into account. This has been done by Kushida, Benedek and Bloembergen (KBB),[2] who have come to the following relation:

$$\nu_Q(T) = a_0 + a_1T + a_2T^{-1}, \tag{5}$$

$$a_0 = \nu_Q^S, \tag{6}$$

$$a_1 = -\frac{3}{2}k\nu_Q^S\sum_{i=1}^{M}\frac{A_i}{\omega_i^2}, \tag{7}$$

$$a_2 = -\frac{\hbar^2}{8k}\nu_Q^S\sum_{i=1}^{M}A_i, \tag{8}$$

where $\nu_Q^S$ is the resonance frequency in a fictitious "static" lattice, $\omega_i$ is the frequency of the $i$-th lattice vibrational mode, and $A_i$ is a coefficient which for librations is equal to the reciprocal of the relevant moment of inertia.

A few years later Brown[3] took into account anharmonicity of librations, assuming a linear temperature dependence of librational frequency:

$$\omega_i = \omega_i^0(1 - g_iT). \tag{9}$$

Moreover Brown limited his considerations to the appropriately high temperatures for which the term $a_2T^{-1}$ of Eq. 5 can be neglected. Under this assumption he obtained:

$$\nu_Q(T) = a_0 + a_1T + a_2T^2, \tag{10}$$

$$a_0 = \nu_Q(0), \tag{11}$$

$$a_1 = -\frac{3}{2}k\nu_Q(0)\sum_{i=1}^{M}\frac{A_i}{(\omega_i^0)^2}, \tag{12}$$

$$a_2 = -3k\nu_Q(0)\sum_{i=1}^{M}\frac{g_iA_i}{(\omega_i^0)^2}. \tag{13}$$

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As this dependence describes quite well most of experimentally obtained data $\nu_Q(T)$ for the temperatures above 77 K, we attempted to extend this approach to study the influence of molecular motions on NQR frequency in the temperatures lower than 77 K. After the calculations similar to those of Brown[3] and taking into account the term $a_2T^{-1}$ in Eq. 5 we have come to:

$$\nu_Q(T) = a_0 + a_1T + a_2T^2 + a_3T^{-1}, \tag{14}$$

$$a_0 = \nu_Q^S, \tag{15}$$

$$a_1 = -\frac{3}{2}k\nu_Q^S\sum_{i=1}^{M}\frac{A_i}{(\omega_i^0)^2}, \tag{16}$$

$$a_2 = -3k\nu_Q^S\sum_{i=1}^{M}\frac{g_iA_i}{(\omega_i^0)^2}, \tag{17}$$

$$a_3 = -\frac{\hbar^2}{8k}\nu_Q^S\sum_{i=1}^{M}A_i. \tag{18}$$

In IR and Raman spectroscopy the square dependence of librational frequency on temperature has been observed for a significant number of compounds:

$$\omega_i = \omega_i^0(1 - g_iT - f_iT^2). \tag{19}$$

Taking into account Eq. 19 in our calculations we obtain:

$$\nu_Q(T) = a_0 + a_1T + a_2T^2 + a_3T^3, \tag{20}$$

$$a_0 = \nu_Q(0), \tag{21}$$

$$a_1 = -\frac{3}{2}k\nu_Q(0)\sum_{i=1}^{M}\frac{A_i}{(\omega_i^0)^2}, \tag{22}$$

$$a_2 = -3k\nu_Q(0)\sum_{i=1}^{M}\frac{g_iA_i}{(\omega_i^0)^2}, \tag{23}$$

$$a_3 = -3k\nu_Q(0)\sum_{i=1}^{M}\frac{f_iA_i}{(\omega_i^0)^2}. \tag{24}$$

Equation 20 can be applied to appropriately high temperatures similarly as the Brown's relation—Eq. 10. Extending the above treatment of the influence of librations on NQR spectrum to very low temperatures we obtain:

$$\nu_Q(T) = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^{-1}, \tag{25}$$

$$a_0 = \nu_Q^S, \tag{26}$$

$$a_1 = -\frac{3}{2}k\nu_Q^S\sum_{i=1}^{M}\frac{A_i}{(\omega_i^0)^2}, \tag{27}$$

$$a_2 = -3k\nu_Q^S\sum_{i=1}^{M}\frac{g_iA_i}{(\omega_i^0)^2}, \tag{28}$$

$$a_3 = -3k\nu_Q^S\sum_{i=1}^{M}\frac{f_iA_i}{(\omega_i^0)^2}, \tag{29}$$

$$a_4 = -\frac{\hbar^2}{8k}\nu_Q^S\sum_{i=1}^{M}A_i. \tag{30}$$

As follows from the above theories, the accurate fit of experimentally obtained NQR frequencies vs. temperature to the relations found allows one to determine the librational frequencies and the corresponding moments of inertia of the molecules studied.

The other NQR spectroscopy parameters—the line width ($\delta\nu_Q$) and spin-lattice relaxation time ($T_1$)—are sensitive to greater changes in electric field gradient caused by hindered rotations of (i) atomic groups or molecules including the resonant nuclei or (ii) atomic groups or molecules situated in the neighborhood of the resonant nuclei. In general, we can state that the line width is a resultant effect of static broadening (both electric and magnetic) associated with a crystal lattice, and dynamic broadening associated with some kind of motion (e.g., with a hindered rotation). If the resonant nuclei rotate, the line becomes broadened, and if neighboring groups containing protons rotate the NQR line narrows. In general, the line width observed can be expressed as:[4,5]

$$(\delta\nu_Q)^{observ.} = (\delta\nu_Q)^{static} + (\delta\nu_Q)^{narrow.} + (\delta\nu_Q)^{broad.}, \tag{31}$$

$$(\delta\nu_Q)^{narrow.} = -A\exp(-E_a'/RT), \tag{32}$$

$$(\delta\nu_Q)^{broad.} = B\exp(-E_a/RT), \tag{33}$$

where $A$ and $B$ are constants and $E_a$ and $E_a'$ are the activation energies for hindered rotations analyzed, $R$ is the gas constant.

Let us now consider the nuclear quadrupole spin-lattice relaxation. According to Bayer[1] as well as Woessner and Gutowsky[6] the fluctuations of electric field gradient caused by librational motions lead to the following relation between the relaxation time $T_1$ and temperature ($T$):

$$T_1^{-1} = aT^n \tag{34}$$

where $a$ is a constant and $n\approx 2$.

Abrupt changes in electric field gradient due to hindered rotation of molecular groups containing quadrupole nuclei (e.g., $CCl_3$ group) lead to the exponential temperature dependence of the relaxation time:[7]

$$T_1^{-1} = b\exp(-E_a/RT) \tag{35}$$

where $b$ is a constant, $E_a$ is the activation energy for hindered rotation.

If atomic groups in the neighborhood of the resonating nuclei undergo a rotation with a frequency close to the observed NQR freguency, then in the temperature dependence of $T_1$ a so-called modulation minimum is observed that can be described by the formula:[6,8]

$$T_1^{-1} = [d\exp(E_a'/RT) + g\exp(-E_a'/RT)]^{-1} \tag{36}$$

where

$$d = 3\tau_0\left(\frac{q'_{zz}}{q_{zz}}\right)^{-2}, \quad (37)$$

$$g = \frac{3}{\omega_Q^2\tau_0}\left(\frac{q'_{zz}}{q_{zz}}\right)^{-2}. \quad (38)$$

$E'_a$ is the activation energy for hindered rotation of the corresponding molecular groups, $\tau_0$ is the correlation time at infinitely high temperature, and $q'_{zz}$ is the contribution of motions of adjacent groups or molecules to the whole electric field gradient $q_{zz}$.

## The Application of Microcomputer in Analysis of NQR Data

After discussion of the present theories we may state that in most cases the fit of experimental data to the above relations is sufficient for determination of searched parameters. All these relations have been reduced to a few general equations:

$$y = a - b[\exp(c/x) - 1]^{-1} \quad (39)$$

$$y = a_0 + a_1x + a_2x^2 + \cdots + a_px^p \quad (40)$$

$$y = a_0 + a_1x + a_2x^2 + \cdots + a_{p-1}x^{p-1} + a_px^{-1} \quad (41)$$

$$y^{-1} = ax^n \quad (42)$$

$$y^{-1} = b\exp(-c/x) \quad (43)$$

$$y^{-1} = ax^n + b\exp(-c/x) + A[d\exp(f/x) + g\exp(-f/x)]^{-1} + B[k\exp(m/x) + l\exp(-m/x)]^{-1} \quad (44)$$

$$y = h + d\exp(f/x) + g\exp(-m/x) \quad (45)$$

Eqs. 39—41 refer to the NQR frequency, Eqs. 42—44 to the $T_1$ relaxation time and Eq. 45 to the NQR line width.

A SINCLAIR ZX81 microcomputer with a memory extended to 64 kB and with High Resolution Graphics add-on was used to do all the calculations. The programs prepared in ZX81 BASIC are based on the standard least squares approximation and the gradient method. The programs applied allow to determine the parameters of interest as well as the quality of the fit by error analysis. The quality of the fit may also be observed on the monitor, as the fit curve is displayed together with the experimental points. The diagrams may be plotted in the following systems of coordinates: $x$, $\ln x$, $1/x$, $x^n$ (the same refers to the $y$ axis). Each diagram seen on the monitor may be copied by a printer. Experimental data may be entered manually or loaded from a cassette-recorder.

## An Example of NQR Data Analysis

The computer analysis will be demonstrated by results obtained from $^{35}$Cl NQR studies of *p,p'*-DDT/1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane; $CCl_3CH(C_6H_4Cl)_2$/. The $^{35}$Cl NQR data for *p,p'*-DDT include all the effects discussed previously. We deal here with hindered rotation of the resonant nuclei ($CCl_3$ groups) and with the influence of rotating neighboring groups (phenyl rings). The motion of phenyl rings leads to a narrowing of $^{35}$Cl NQR line, while the hindered rotation of $CCl_3$ groups is observed as a rapid broadening of the resonance lines. In the temperature dependences of the relaxation times we observe two modulation minima due to the rotating phenyl rings. Molecular dynamics of *p,p'*-DDT and the results of $^{35}$Cl NQR studies are reported in more

Table 1. Parameters of the Fit of Experimental $\nu_Q^3(T)$ Values for *p,p'*-DDT to the Proper Theories-Formulas: Eqs. 1, 5, 10, 14, 20, and 25. For the Sake of Clarity All Parameters Standing at $T^{-1}$ in Formulas Are Denoted by a Common Symbol d

| Formula | Notation of $\nu_Q(T)$ curves in Figs. 1—6 | $a_0$ or $a$ | $a_1$ | $a_2$ |
|---|---|---|---|---|
| | | MHz | $10^{-3}$ MHz K$^{-1}$ | $10^{-6}$ MHz K$^{-2}$ |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3+dT^{-1}$ | F | 38.629 | −1.606 | −1.293 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+dT^{-1}$ | D | 38.599 | −1.164 | −3.373 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2$ | A | 38.583 | −1.051 | −3.578 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3$ | E | 38.582 | −1.001 | −3.708 |
| $\nu_Q(T)=a-\frac{b}{\exp(c/T)-1}$ | B | 38.538 | — | — |
| $\nu_Q(T)=a_0+a_1T+dT^{-1}$ | C | 38.797 | −2.854 | — |

| Formula | $a_3$ | $d$ | $b$ | $c$ | Standard deviation |
|---|---|---|---|---|---|
| | $10^{-9}$ MHz K$^{-3}$ | MHz K | MHz | K | kHz |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3+dT^{-1}$ | −2.990 | −0.799 | — | — | 2.91 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+dT^{-1}$ | — | −0.340 | — | — | 3.51 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2$ | — | — | — | — | 3.96 |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3$ | +0.210 | — | — | — | 3.98 |
| $\nu_Q(T)=a-\frac{b}{\exp(c/T)-1}$ | — | — | 0.827 | 257.8 | 15.08 |
| $\nu_Q(T)=a_0+a_1T+dT^{-1}$ | — | −3.914 | — | — | 24.39 |

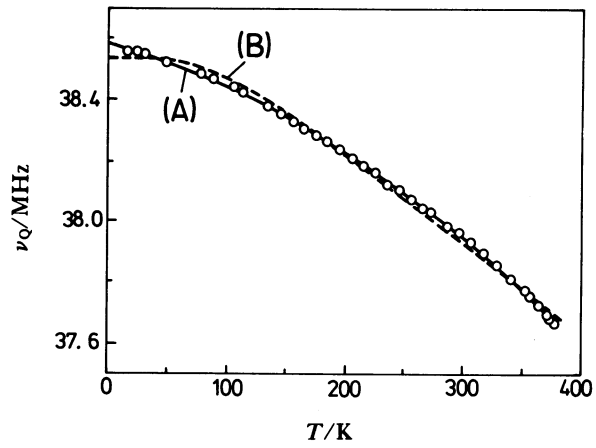


Fig. 1. Comparison of the fits of temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT to: (A)—Brown's relation (Eq. 10 or 40 for $p$=2), (B)—Bayer's relation (Eq. 1 or 39); O—experimental points.

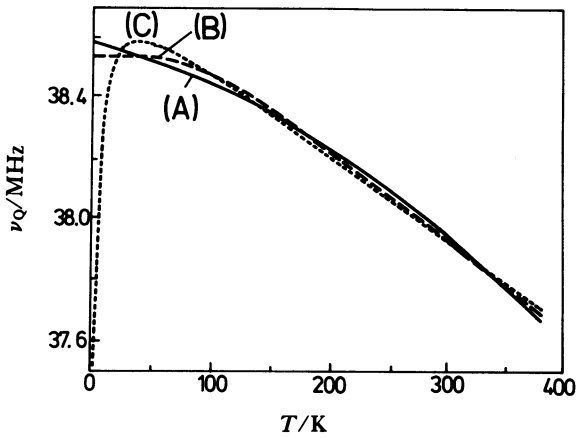


Fig. 2. Comparison of the fits of temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT to: (A)—Brown's relation (Eq. 10 or 40 for $p$=2), (B)—Bayer's relation (Eq. 1 or 39), (C)—KBB relation (Eq. 5 or 41 for $p$=2).

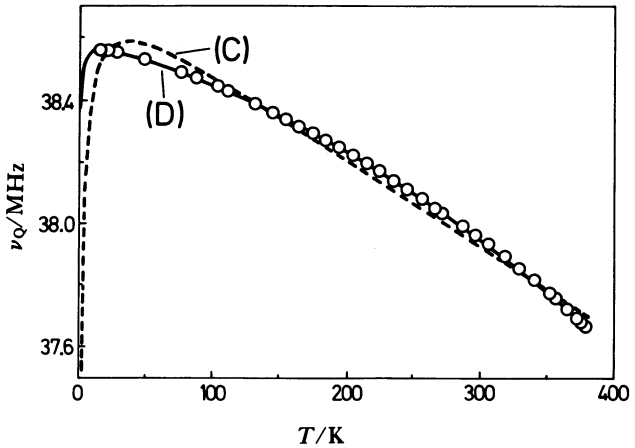


Fig. 3. Comparison of the fits of temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT to: (C)—KBB relation (Eq. 5 or 41 for $p$=2), (D)—Eq. 14 or 41 for $p$=3; O—experimental points.

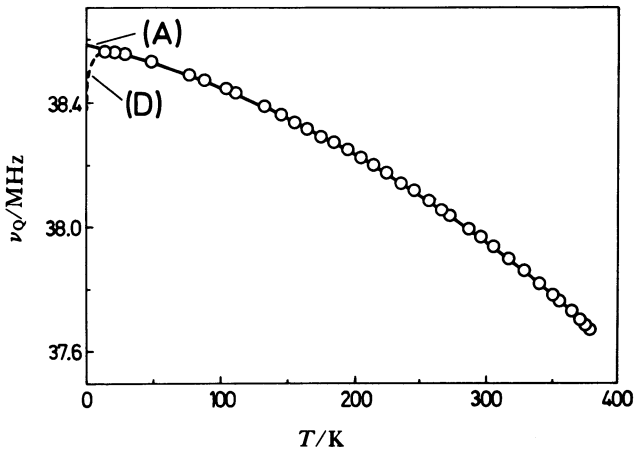


Fig. 4. Comparison of the fits of temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT to: (A)—Brown's relation (Eq. 10 or 40 for $p$=2), (D)—Eq. 14 or 41 for $p$=3; O—experimental points.

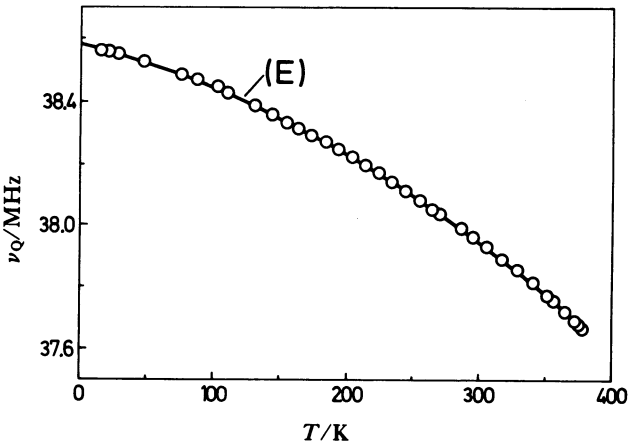


Fig. 5. Temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT. O—experimental points; solid line (E)—fit to Eq. 20 or 40 for $p$=3.

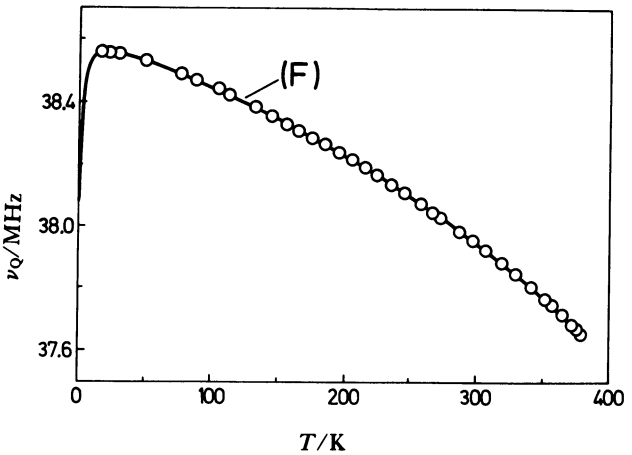


Fig. 6. Temperature dependence of $^{35}$Cl NQR frequency for $\nu_Q^3$ line in $p,p'$-DDT. O--experimental points; solid line (F)—fit to Eq. 25 or 41 for $p$=4 (best fit).

Table 2. The Values of Parameters Determining Temperature Dependence of Mean Librational Frequency ($\nu_l$) of the Chlorine Atom (of $CCl_3$ Group in $p,p'$-DDT) Obtained from the Fit of Experimental Data $\nu_Q^3(T)$ to Individual Theories-Formulas: Eqs. 10, 14, 20, and 25

| Formula | Determined parameter | | | Notation of $\nu_l(T)$ in Fig. 7 |
|---|---|---|---|---|
| | $\nu_1^0$ | $g$ | $f$ | |
| | $cm^{-1}$ | $10^{-4}\,K^{-1}$ | $10^{-7}\,K^{-2}$ | |
| | | $\nu_l=\nu_l^0(1-gT)$ | | |
| $\nu_Q(T)=a_0+a_1T+a_2T^2$ | 112.85 | 17.028 | — | (1) |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^{-1}$ | 107.26 | 14.495 | — | (2) |
| | | $\nu_l=\nu_l^0(1-gT-fT^2)$ | | |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3$ | 114.01 | 18.009 | −1.020 | (3) |
| $\nu_Q(T)=a_0+a_1T+a_2T^2+a_3T^3+a_4T^{-1}$ | 91.32 | 4.024 | 9.308 | (4) |

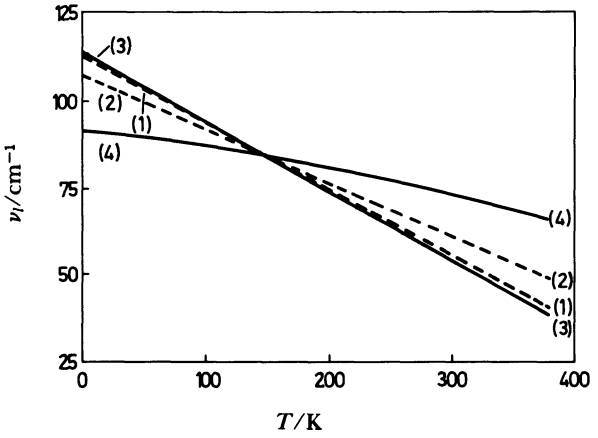


Fig. 7. Temperature dependence of mean librational frequency ($\nu_l$) for chlorine atom (of the $CCl_3$ group in $p,p'$-DDT) obtained from fitting the $\nu_Q^3(T)$ data to the proper theories-formulas: Eqs. 10, 14, 20, and 25. The line (1) and (2) represent the dependence $\nu_l=\nu_l^0(1-gT)$ while the lines (3) and (4) stand for $\nu_l=\nu_l^0(1-gT-fT^2)$. The values of $\nu_l^0$, $g$ and $f$ are given in Table 2.

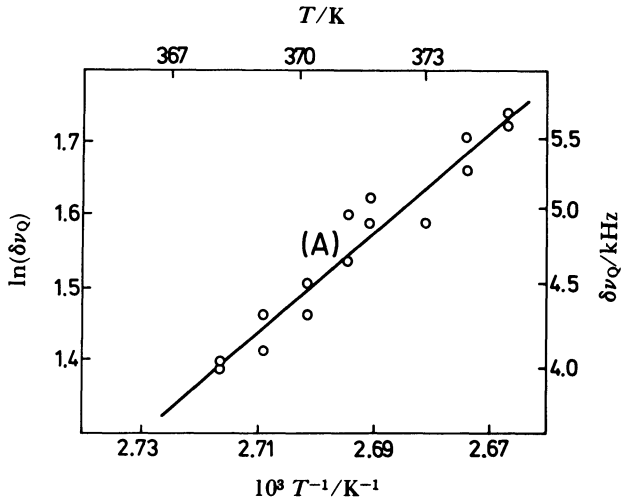


Fig. 8. Temperature dependence of $^{35}Cl$ NQR line width for rotating chlorines of the $CCl_3$ group (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in $p,p'$-DDT). O—experimental points; solid line (A)—fit to Eq. 33 or 45 for $h=0$ and $d=0$.

detail in Refs. 9—13. In this paper we shall concentrate on the analysis of some experimental results.

We shall illustrate the temperature dependence of $^{35}Cl$ NQR frequency for the $\nu_Q^3$ line which is one of the five resonance lines observed for $p,p'$-DDT.[9-13] The parameters of the fit of the experimental dependence $\nu_Q=\nu_Q^3=f(T)$ to individual theories — formulas are given in Table 1 while Figs. 1—6 illustrate the quality of the fits. The formulas in Table 1 are arranged according to increasing standard deviation. As follows from Table 1 the best agreement between the experimental data and the three basic theories (Bayer, KBB, and Brown) was obtained for Brown's formula, Figs. 1 and 2. Thus, it validated the introduction of anharmonicity of vibrations through the linear temperature dependence of their frequencies. The fit improves when we modify the Brown's dependence to extend its validity also at relatively low temperatures, Eq. 14, see curves (D) in Figs. 3 and 4. However, the best fit has been obtained by assuming the square temperature dependence of librational frequency, Eq. 25, see curve (F) in Fig. 6 and Table 1. Despite some really good fits of $\nu_Q(T)$ obtained, none of the equations applied does describe the experimental dependence sufficiently well in very low temperatures, below 20 K. Nevertheless, using these fits we can find the appropriate moments of inertia, librational frequencies and the parameters describing the temperature dependence of librational frequency. Table 2 presents the appropriate parameters for linear and square temperature dependences of mean librational frequency of the Cl atom considered, while Fig. 7 illustrates $\nu_l(T)$ dependences. Curve (4) in Fig. 7 shows the dependence $\nu_l(T)$ obtained from the best fit of $\nu_Q(T)$. The square temperature dependence of librational frequency presented as curve (4) in Fig. 7 is the closest approximation of the real situation for the $p,p'$-DDT. A detailed analysis of other parameters obtained from individual fits of $\nu_Q(T)$ is given in Refs. 9, 10, and 13.

The width of the resonance line ($\delta\nu_Q$) may be analyzed with the help of the computer program finding the fit of $\delta\nu_Q(T)$ to Eq. 45. As an example we shall analyze the width of the resonance lines due to

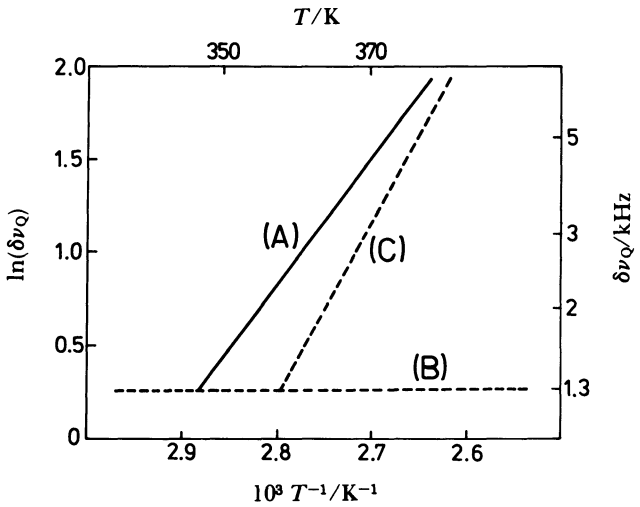


Fig. 9. Separation of $^{35}Cl$ NQR line width observed (line (A) in Figs. 8 and 9) into line width related to hindered rotation of $CCl_3$ groups (line (C)) and line width being the resultant effect of static line width and dynamical narrowing due to hindered rotation of phenyl rings in *p,p'*-DDT (line (B)).

$$(\delta\nu_Q)^{\text{observed}} = (\delta\nu_Q)' + B\exp(-E_a/RT)$$
(A) (B) (C)

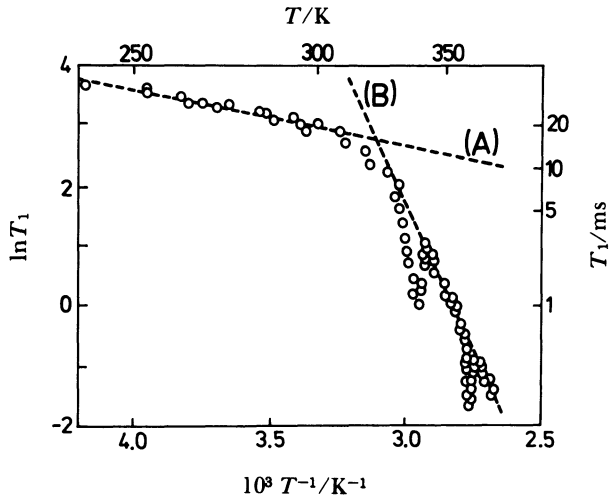


Fig. 10. Temperature dependence of nuclear quadrupole spin-lattice relaxation time ($T_1$) (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in *p,p'*-DDT). O—experimental points; (A)—fit function taking into account only librations (Eq. 34 or 42); (B)—fit function taking into account only hindered rotations of $CCl_3$ groups (Eq. 35 or 43).

chlorine atoms of $CCl_3$ group in *p,p'*-DDT. As a result of growing rate of hindered rotation of $CCl_3$ group with increasing temperature the lines undergo significant broadening, which is shown in Fig. 8. The separation of line width being the resultant effect of static line width and dynamical narrowing from the observed line width leads to obtaining the pure effect of line broadening due to hindered rotation of $CCl_3$ group (see Fig. 9). This procedure also allows us to determine the activation energy for hindered rotation of $CCl_3$ group which in the case considered is 77.9 kJ mol$^{-1}$. The computer analysis of resonance line widths in *p,p'*-DDT is given in more detail in Refs. 9, 10, and 13.

As an example of the computer analysis of quadrupole relaxation time $T_1$ let us consider the relaxation times studied on chlorine nuclei of $CCl_3$ group in *p,p'*-DDT. We shall consider the temperature range from 200 to 378 K, within which there are several relaxation mechanisms: the mechanism associated with librations of Cl atoms of $CCl_3$ group, another associated with hindered rotation of $CCl_3$ groups and the modulation mechanism associated with hindered rotation of the two dynamically nonequivalent groups of phenyl rings. All these mechanisms influence the measured relaxation times $T_1$:

$$(T_1^{-1})^{\text{observed}} = (T_1^{-1})^{\text{librations}} + (T_1^{-1})^{CCl_3\ \text{rot.}} + (T_1^{-1})_{\text{I}}^{\text{modul.}} + (T_1^{-1})_{\text{II}}^{\text{modul.}} \quad (46)$$

Using Eqs. 34—36 we come to:[12]

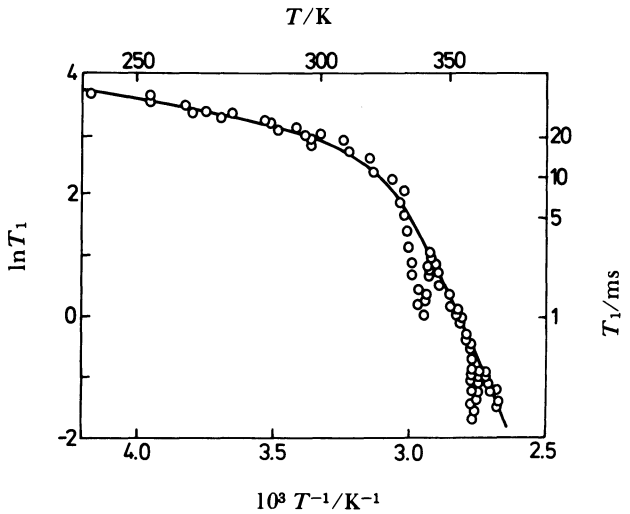


Fig. 11. Temperature dependence of nuclear quadrupole spin-lattice relaxation time ($T_1$) (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in *p,p'*-DDT). O—experimental points; solid line-fit function taking into account both librations and hindered rotations of $CCl_3$ groups (Eq. 44 for $A$=0 and $B$=0).

$$(T_1^{-1})^{\text{observed}} = aT^n + b\exp(-E_a/RT) + [d\exp(E_a'/RT) + g\exp(-E_a'/RT)]^{-1} + [k\exp(E_a''/RT) + l\exp(-E_a''/RT)]^{-1} \quad (47)$$

The most important parameters in the above equation are activation energies for hindered rotation of individual atomic groups: $E_a$ for $CCl_3$ group, $E_a'$ and $E_a''$ for the two groups of phenyl rings. Figures 10—14 show the computer fit of the experimentally obtained $T_1(T)$ to Eqs. 47 and 44 where various mechanisms are

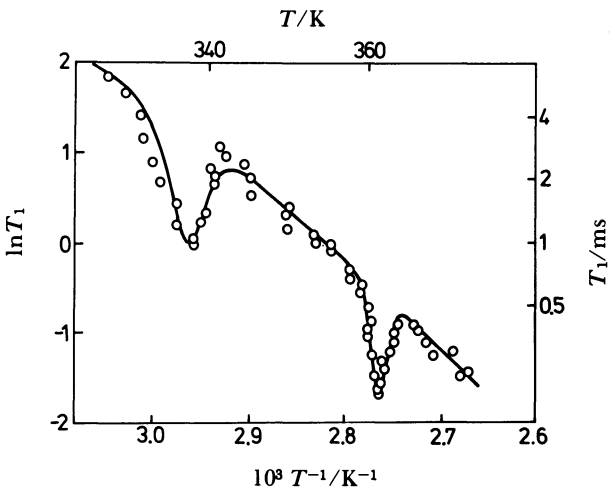


Fig. 12. Temperature dependence of nuclear quadrupole spin-lattice relaxation time ($T_1$) (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in *p,p'*-DDT). O—experimental points; solid line-fit function taking into account librations, hindered rotations of $CCl_3$ groups and the influence of rotating two nonequivalent phenyl groups (two modulation minima) (Eq. 44 for $A$=1 and $B$=1 or Eq. 47).

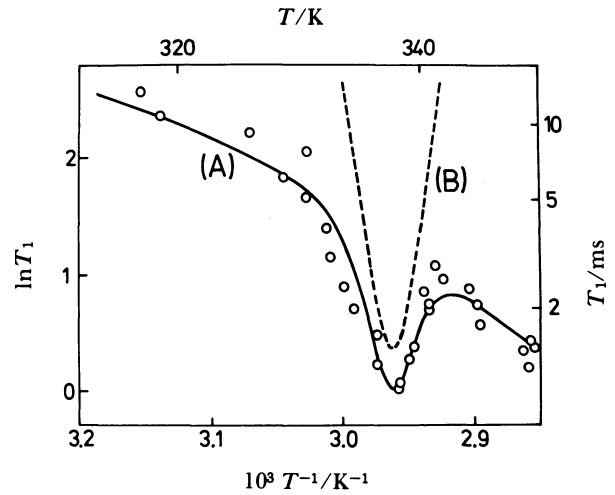


Fig. 13. Temperature dependence of nuclear quadrupole spin-lattice relaxation time ($T_1$) (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in *p,p'*-DDT)—the first modulation minimum. O—experimental points; (A)—fit function taking into account librations, hindered rotations of $CCl_3$ groups and the influence of rotating phenyl rings (Eq. 44 for $A$=1 and $B$=1 or Eq. 47); (B)—function describing only the modulation effect due to rotation of one group of phenyl rings (Eq. 36 or 44 for $a$=0, $b$=0, $A$=1, and $B$=0).

taken into account. From these fits we determined the following activation energies: $E_a$=86.6 kJ mol$^{-1}$, $E_a'$= 84.5 kJ mol$^{-1}$, and $E_a''$=91.0 kJ mol$^{-1}$.[12] Moreover, derived mathematical expression for the curve $T_1^{-1}=f(T)$ allows us to determine accurately the temperature at which the relaxation time reaches its minimum value. This, in turn, enables finding activation energy of the atomic group as well as contribution of the modulated (due to phenyl rings

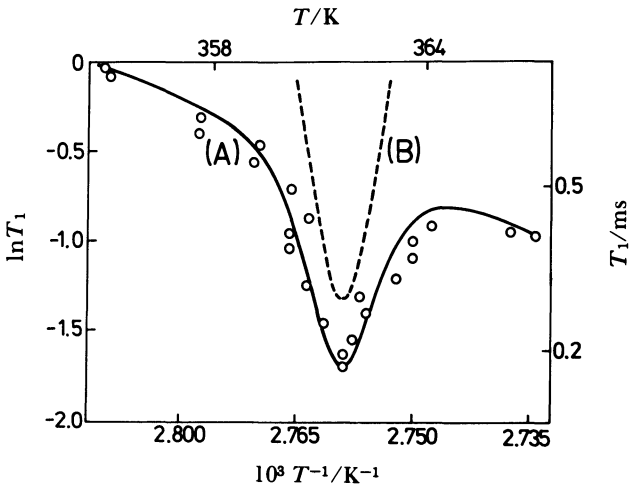


Fig. 14. Temperature dependence of nuclear quadrupole spin-lattice relaxation time ($T_1$) (lines $\nu_Q^3$, $\nu_Q^4$, $\nu_Q^5$ in *p,p'*-DDT)—the second modulation minimum. O—experimental points; (A)—fit function taking into account librations hindered rotations of $CCl_3$ groups and the influence of rotatings (Eq. 44 for $A$=1 and $B$=1 or Eq. 47); (B)—function describing only the modulation effect due to rotation of one (the other than in Fig. 13) group of phenyl rings (Eq. 36 or 44 for $a$=0, $b$=0, $A$=0, and $B$=1).

rotation) $q'_{zz}$ gradient to the total electric field gradient $q_{zz}$ on the chlorine nucleus.[12] Complete analysis of the results obtained from the computer fits of $T_1(T)$ data is given in Refs. 10 and 12.

In conclusion we can say that all kinds of temperature dependences of fundamental parameters in NQR spectroscopy may be described by more or less complex mathematical formulas. Further, it is sufficient to perform an accurate computer fit which may be done even with the help of a personal computer. The parameters determined from the fits are the functions of the physical parameters describing the electronic structure and dynamics of the molecules studied.

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