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High resolution incoherent quasielastic neutron scattering study of molecular reorientations of trimethylacetic acid $(\text{CH}_3)_3\text{CCOOD}$ in its low-temperature phase

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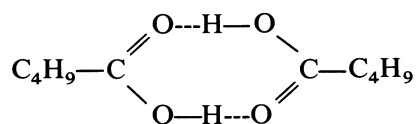
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Résumé. — La diffusion quasi élastique incohérente des neutrons a permis d'étudier les réorientations moléculaires de l'acide triméthylacétique partiellement deutéré $(\text{CH}_3)_3\text{CCOOD}$ dans sa phase basse température. Les mesures ont été effectuées dans un domaine de température allant de 80 K à 254 K, en utilisant une longueur d'onde des neutrons incidents $\lambda = 6,28 \text{ \AA}$. Les spectres quasi élastiques observés peuvent être convenablement décrits par un modèle combinant simultanément des réorientations de 120° des groupements méthyles et t-butyles.

Abstract. — Using the incoherent quasielastic neutron scattering technique, we have studied the molecular reorientations of partially deuterated trimethylacetic acid $(\text{CH}_3)_3\text{CCOOD}$ in its low temperature phase. The measurements were carried out with a sample temperature in the range from 80 K to 254 K, using an incoming neutron wavelength $\lambda = 6.28 \text{ \AA}$. The observed quasielastic spectra are consistent with a model allowing a combination of 120° -reorientations of the methyl and t-butyl groups.

1. **Introduction.** — Trimethylacetic (pivalic) acid, $(\text{CH}_3)_3\text{CCOOH}$ exhibits a plastic phase between $T_i = 280 \text{ K}$ and the melting point $T_m = 309 \text{ K}$. X-ray studies [1, 2] have established that this phase has a f.c.c. crystal structure (space group $\text{Fm}\bar{3}\text{m}$), with a unit cell parameter $a = 8.82 \text{ \AA}$ and contains four molecules. Below 280 K the elementary cell is triclinic [3] (space group $\text{P}\bar{1}$, $Z = 4$, $a = 9.31 \text{ \AA}$, $b = 10.68 \text{ \AA}$, $c = 6.56 \text{ \AA}$, $\alpha = 101^\circ 29$, $\beta = 96^\circ 05$, $\gamma = 104^\circ 7$) and the existence of hydrogen bonded dimers :



is clearly shown (Fig. 1).

Taking into account the molecular symmetry, the structure of the plastic phase is only possible if the molecules reorient between several equilibrium positions which correspond to the dimers aligned with the twelve $[110]$ directions of the cubic cell. The analysis of these motions has already been performed by means of different techniques.

In 1971, Jackson and Strange [4] measured the nuclear magnetic spin relaxation times T_1 , T_2 and $T_{1\rho}$ for methyl and acid protons throughout the plastic

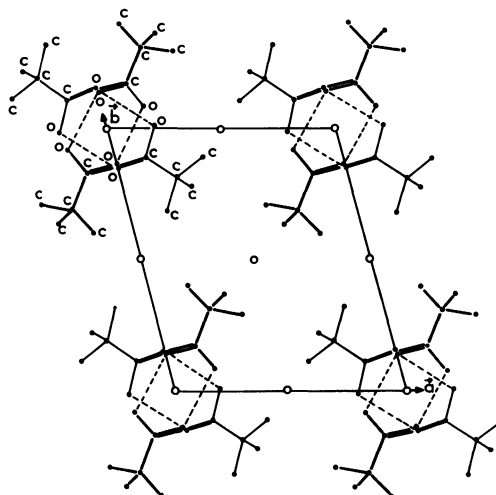


Fig. 1. — The triclinic structure of $(\text{CH}_3)_3\text{CCOOH}$ in the low temperature phase as obtained from an X-ray study [3]. Dashed lines indicate the hydrogen bonds.

crystalline phase. From $T_{1\rho}$ and T_2 for the methyl protons they deduced translational self diffusion coefficients which were in fair agreement with previous radiotracer measurements [5-7]. $T_{1\rho}$ and T_2 of the acid protons show a more rapid translational motion through the lattice than the molecules. This effect has been interpreted in terms of a quasi isotopic reorientation of the pivalic acid molecules involving the making and breaking of dimers.

In 1976, Albert *et al.* [8] investigated both low and high temperature phases, using pulsed and continuous wave proton magnetic resonance methods. Above the transition at 280 K, T_1 and $T_{1\rho}$ measurements show, respectively, an overall molecular tumbling and a self diffusion. For the low temperature phase of the partially deuterated form, $(\text{CH}_3)_3\text{CCOOD}$, the second moment and spin lattice relaxation time of the protons are in agreement with a combination of methyl group and t-butyl group reorientations having activation energies of 2.35 ± 0.15 and 4.00 ± 0.25 kcal/mole, respectively.

In 1977, Leadbetter and Turnbull [9] measured the incoherent quasielastic neutron scattering of this compound. However, poor instrumental resolution did not enable them to distinguish between several possible models for molecular motions.

Recently, we have performed additional quasielastic neutron scattering experiments with improved experimental conditions. To distinguish between various models for molecular motions in the plastic phase, a set of full or partially deuterated compounds was used in order to enhance, or reduce, the scattered intensity, arising from the different parts of the molecule. The measurements made with the partially deuterated compound $(\text{CH}_3)_3\text{CCOOD}$ enabled us to conclude that no tumbling process occurs in the plastic phase on a time scale of 10^{-11} s (in agreement with the value $\tau = 2 \times 10^{-9}$ s obtained by Albert *et al.* [8]). The important quasielastic broadening has to be interpreted from uniaxial rotations of the whole tertibutyl group and of the individual CH_3 groups. We shall report on these experiments in more detail elsewhere. As in the low temperature phase a small broadening is still visible, in accordance with the results of the NMR study, another quasielastic experiment was performed in this phase, using the high resolution backscattering spectrometer, IN10, of the Institut Laue-Langevin. These results are reported here.

2. Experimental. — IQNS measurements of $(\text{CH}_3)_3\text{CCOOD}$ were carried out at four temperatures: $T = 80$ K, 178 K, 215 K and 254 K. The low temperature crystalline structure is triclinic. Great care was taken to avoid Bragg reflexions. The incident neutron wavelength was $\lambda = 6.28 \text{ \AA}$, corresponding to an energy $E = 2.073$ meV. Three analysers were set at scattering angles $2\theta = 52^\circ$, 73° and 101° (momentum transfer $Q = 0.88 \text{ \AA}^{-1}$, 1.19 \AA^{-1} and 1.54 \AA^{-1} , respectively) and partially occulted with cadmium, giving only 6 degrees of angular width. Another analyser was

used at small scattering angle $2\theta = 12^\circ$ ($Q = 0.21 \text{ \AA}^{-1}$). The resolution was about 1 \mu eV (fwhm). Polycrystalline pivalic acid was held in a slab-shaped container made in circular geometry 0.3×50 mm in size, with walls of thin aluminium plates. A liquid nitrogen cryostat was used and deviations in the temperature stability were less than half a degree. In all the experiments the angle between the plane of the sample and the incident neutron beam was 125° .

3. The scattering law and the models. — Due to the large incoherent cross section of hydrogen in a IQNS experiment, only the t-butyl contribution to the scattering is relevant. The molecular motions which are compatible with the triclinic lattice are 120° rotations of the methyl groups, eventually together with 120° rotations of the whole tertibutyl group (Fig. 2). The case of 120° rotations of the t-butyl alone is unlikely to occur and will not be considered here. It can be taken as a realistic assumption that the two kinds of rotations above are not correlated. We can use the method indicated by Rigny [10] Thibaudier and Volino [11], [12]. Let us denote by τ_M^{-1} the probability of a $\pm 120^\circ$ jump for a methyl group and by τ_B^{-1} the corresponding probability for the whole t-butyl group. Four correlation times are involved :

$$\tau_0^{-1} = 0, \quad (1a)$$

$$\tau_1^{-1} = \frac{3}{2} \tau_M^{-1}, \quad (1b)$$

$$\tau_2^{-1} = \frac{3}{2} \tau_B^{-1}, \quad (1c)$$

$$\tau_3^{-1} = \frac{3}{2} \tau_M^{-1} + \frac{3}{2} \tau_B^{-1}. \quad (1d)$$

The rotational incoherent scattering function, $S_{\text{inc}}^R(Q, \omega)$, now takes the form :

$$S_{\text{inc}}^R(Q, \omega) = a_0(Q) \delta(\omega) + \sum_{\mu=1}^3 a_\mu(Q) \mathcal{L}_\mu(\omega) \quad (2a)$$

with

$$\mathcal{L}_\mu(\omega) = \frac{1}{\pi} \frac{\tau_\mu}{1 + \omega^2 \tau_\mu^2}. \quad (2b)$$

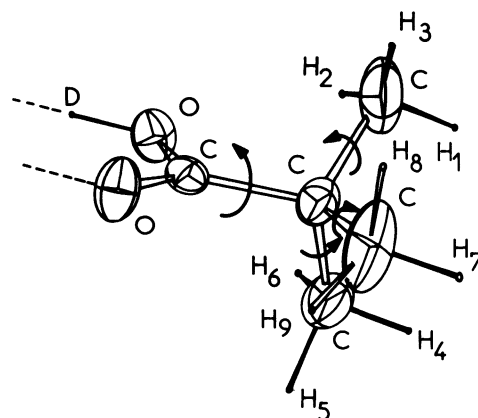


Fig. 2. — The trimethylacetic acid molecule. Positions of the hydrogen atoms have been deduced from the low temperature phase X-ray study [3]. Possible rotations are indicated by arrows.

Table I. — List of all possible distances R_{ij} between equilibrium positions of an individual proton in the case of a model allowing both methyl and *t*-butyl rotations. These can be reduced to a set of 6 different values. The positions i and j are displayed in figure 2.

$r_1 = 0$	$= R_{ii} \quad i = 1, 2, \dots, 9$
$r_2 = 1.714$	$= R_{12} = R_{13} = R_{32} = R_{45} = R_{46} = R_{56} = R_{78} = R_{79} = R_{89}$
$r_3 = 2.482$	$= R_{14} = R_{17} = R_{26} = R_{38} = R_{47} = R_{59}$
$r_4 = 3.016$	$= R_{16} = R_{18} = R_{24} = R_{37} = R_{49} = R_{58}$
$r_5 = 3.654$	$= R_{15} = R_{19} = R_{25} = R_{27} = R_{28} = R_{34} = R_{36} = R_{39} = R_{48} = R_{58} = R_{67} = R_{69}$
$r_6 = 4.196$	$= R_{29} = R_{35} = R_{68}$

The elastic and quasielastic structure factors $a_\mu(Q)$ can be calculated from the relation [11], [12]

$$a_\mu(Q) = \frac{1}{9} \sum_\nu \sum_\eta \chi_\mu^\nu \chi_\mu^\eta \sum_{B_\nu} \sum_{M_\eta} j_0(Q | \mathbf{r} - B_\nu M_\eta \mathbf{r} |). \quad (3)$$

The sums over ν and η run over the classes of the C_3 -symmetry rotation group for both *t*-butyl and methyl. These rotations are denoted by B_ν and M_η , respectively. χ_μ^ν and χ_μ^η are their characters in the μ irreducible representation. j_0 is a Bessel spherical function. Table I gives the list of all possible jump distances $| \mathbf{r} - B_\nu M_\eta \mathbf{r} |$ for a proton initially located at \mathbf{r} , after the two successive M_η and B_ν rotations.

Explicit expressions of the structure factors are

given in table II. Their variation as functions of Q is drawn in figure 3. Clearly, $a_1(Q)$ and $a_3(Q)$, which are related to correlation times involving the motion of the methyl groups, mainly contribute at large Q -value ($Q > 1.7 \text{ \AA}^{-1}$). Unfortunately, the occurrence of numerous Bragg reflexions in this Q -range did not allow us to set analysers at large scattering angles. However, we shall see later that this motion is fast enough to be observable at lower Q -values, even with a small contribution to the scattering law.

Assuming the existence of methyl rotations alone, we put $\tau_B^{-1} = 0$ and the set of equations (1) above reduces to :

$$\tau_0^{-1} = 0 \quad (4a)$$

$$\tau_1^{-1} = \frac{3}{2} \tau_M^{-1}. \quad (4b)$$

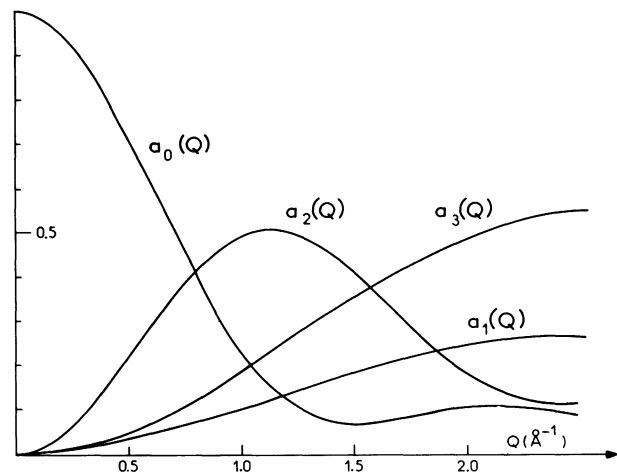


Fig. 3. — Variation of the elastic (EISF) and quasielastic structure factors as function of Q in the case of a model allowing for both methyl and *t*-butyl 120° jumps.

The corresponding structure factors are obtained from

$$A_0(Q) = a_0(Q) + a_2(Q), \quad (5a)$$

$$A_1(Q) = a_1(Q) + a_3(Q) = 1 - A_0(Q). \quad (5b)$$

These could also be obtained directly from the general relation in the case of a uniaxial rotation among N equilibrium positions equally spaced on a circle (see for example eq. (24) in [13]).

4. Results. — Calculation of an experimental EISF by graphically separating the experimental spectra into an elastic and a quasielastic part is rather inaccurate, figures 4a, 4b and 4c show the separation between these two contributions obtained from final refinements. Another more systematic method based on a non-linear least squares was used [14], [15]. Sepa-

Table II. — Expressions of the elastic (EISF) and quasielastic structure factors in the case of methyl and *t*-butyl rotations. The notation $j_0(n)$ is a short hand notation for $j_0(Qr_n)$. The jump distances r_n are listed in table I.

$j_0(x) = \frac{\sin x}{x}$ is a spherical Bessel function.

$$a_0(Q) = \frac{1}{27} [3 + 6j_0(2) + 4j_0(3) + 4j_0(4) + 8j_0(5) + 2j_0(6)],$$

$$a_1(Q) = \frac{1}{27} [6 - 6j_0(2) + 2j_0(3) - 4j_0(4) + 4j_0(5) - 2j_0(6)],$$

$$a_2(Q) = \frac{1}{27} [6 + 12j_0(2) - 4j_0(3) - 4j_0(4) - 8j_0(5) - 2j_0(6)],$$

$$a_3(Q) = \frac{1}{27} [12 - 12j_0(2) - 2j_0(3) + 4j_0(4) - 4j_0(5) + 2j_0(6)].$$

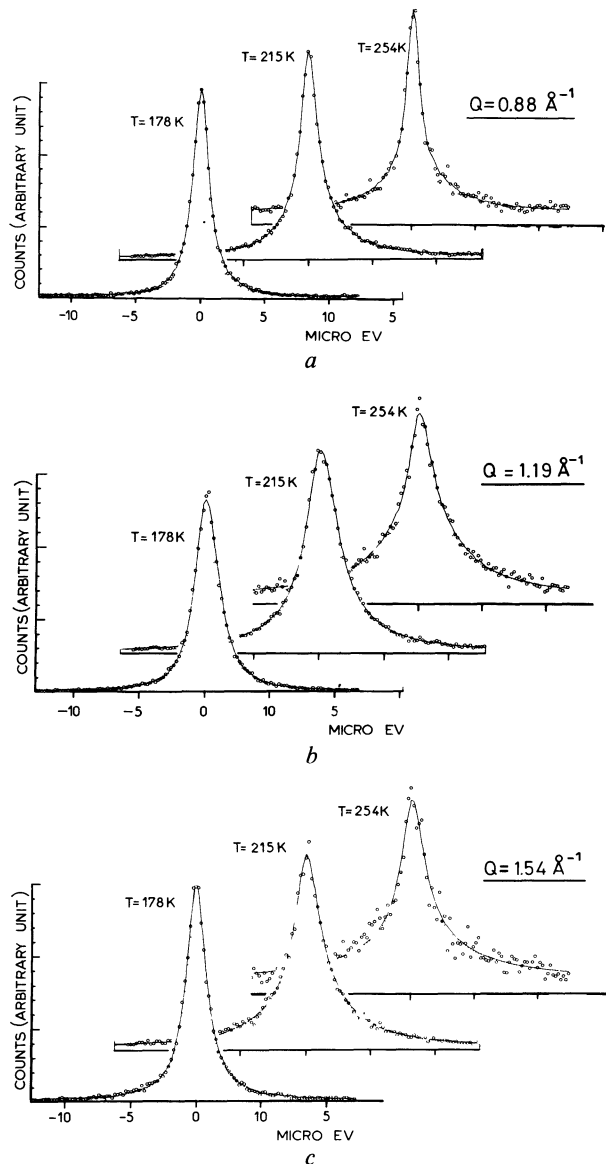


Fig. 4a, 4b, 4c. — Temperature evolution of the IN10 energy spectra. The full curve is the result of the fit to the model allowing a combination of the two motions. The dotted line is the separation between elastic and quasielastic scattering obtained from refinement.

rating the incoherent rotational scattering function, $S_{\text{inc}}^{\text{R}}(Q, \omega)$, into its elastic and quasielastic $\tilde{S}_{\text{inc}}^{\text{R}}(Q, \omega)$ parts

$$S_{\text{inc}}^{\text{R}}(Q, \omega) = A_0(Q) \delta(\omega) + \tilde{S}_{\text{inc}}^{\text{R}}(Q, \omega), \quad (6)$$

the following expression was fitted to each spectrum individually :

$$S_{\text{fit}}^{\text{R}}(Q, \omega) = f(Q) A_0(Q) \delta(\omega) + \frac{1 - f(Q) A_0(Q)}{1 - A_0(Q)} \tilde{S}_{\text{inc}}^{\text{R}}(Q, \omega). \quad (7)$$

The weight parameter, $f(Q)$, controls the amount of elastic scattering. In constructing $S_{\text{fit}}^{\text{R}}(Q, \omega)$ the following three constraints are observed :

- 1) its energy integral is equal to 1,
- 2) $S_{\text{fit}}^{\text{R}}(Q, \omega) = S_{\text{inc}}^{\text{R}}(Q, \omega)$ for $f(Q) = 1$,
- 3) if $f(Q)$ is set $\neq 1$, then only the ratio of elastic to quasielastic intensity is varied, whereas the shape of $\tilde{S}_{\text{inc}}^{\text{R}}(Q, \omega)$ remains unchanged.

The fit of a theoretical model which correctly describes the dynamics of the molecular motion, must result in $f(Q) = 1$ for all scattering angles. However, if $f(Q)$ deviates appreciably from 1, then the product $f(Q) \cdot A_0(Q)$ can nevertheless be expected to tend towards the real (experimental) EISF. Then a more realistic model may be selected.

In the first instance, we tried to analyse the neutron spectra in terms of a model assuming methyl rotations alone. This yields the experimental EISF $f(Q) A_0(Q)$ indicated on figure 5 by circles. It turns out that such a model is insufficient to describe the data, especially at the two higher temperatures, since it predicts an elastic intensity appreciably greater than that observed. This observation indicates that the number of equilibrium positions reached by one individual proton is greater than allowed by this model. The only way to increase this number of positions is to allow the t-butyl group to rotate about its own axis. As a further test, another fit of (7) to the spectra was made, this time based on the model allowing both kinds of rotations. The results are indicated on figure 5, with final values of the $f(Q)$ factors close to 1.

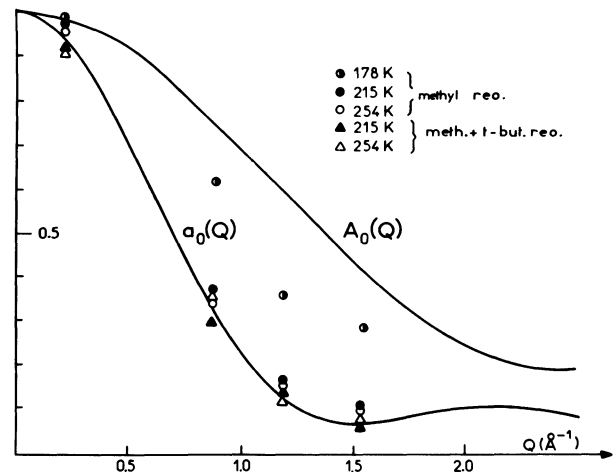


Fig. 5. — Determination of the experimental EISF. Circles are results obtained when assuming methyl rotations alone. Triangles are obtained with a combination of methyl and t-butyl motions.

At 178 K, the experimental values obtained for the EISF tend to the methyl + t-butyl jump model. However, deviations from the methyl jump model alone are smaller and we can conclude that the correlation time related to the t-butyl motion reaches the limit of the instrument energy range.

At 80 K no quasielastic broadening can be observed. Both motions are outside the instrument energy range.

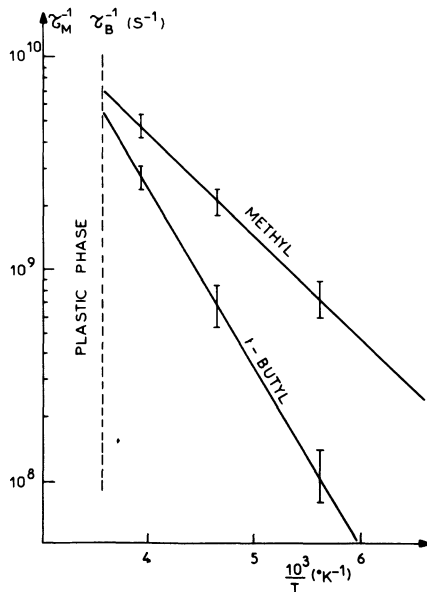


Fig. 6. — Correlation times for the two motions in pivalic acid below the phase transition, versus reciprocal temperature.

From these results, spectra recorded at the same temperature were fitted separately assuming 120° jumps around t-butyl axis together with 120° methyl jumps and putting $f(Q) = 1$ in (7) for all Q values. Good fits were obtained at each temperature (see Fig. 4). The final values of the correlation times were only slightly angle-dependent. Extremal values determine the error bars in figure 6. Effectively, at $T = 178$ K, the value obtained for τ_B is similar to the instrumental resolution ($\tau_B = 10^{-8}$ s, resolution : 2.5×10^{-9} s). However, figure 3 shows that $a_2(Q)$ predominates at our experimental scattering angles, so that τ_B can nevertheless be determined accurately at this temperature. Figure 6 shows the variation of the two correlation times as a function of reciprocal temperature. Two straight lines can be drawn across the experimental points. They correspond to the Arrhenius laws :

$$\tau_M = 2.6 \pm 0.2 \times 10^{-12} \exp(\Delta H_M/RT) \text{ s}, \quad (8a)$$

$$\tau_B = 1.3 \pm 0.1 \times 10^{-13} \exp(\Delta H_B/RT) \text{ s}, \quad (8b)$$

with, respectively, the two activation energies :

$$\Delta H_M = 9.34 \pm 0.15 \text{ kJ/mole for the methyl reorientations,}$$

$$\Delta H_B = 16.7 \pm 0.2 \text{ kJ/mole for the t-butyl reorientations.}$$

In the analysis of their spin-lattice relaxation measurements, Albert *et al.* [8] assume that there are nine equilibrium positions for each internuclear vector, three within each methyl group with three positions for each methyl group. They introduce a correlation time τ_{C1} for jumps within a methyl group and τ_{C2} between different methyl group sites. The following Arrhenius equations for the temperature dependence of the correlation times were obtained :

$$\tau_{C1} = 1.52 \times 10^{-12} \exp(\Delta H_1/RT) \text{ s}, \quad (9a)$$

$$\tau_{C2} = 9.07 \times 10^{-14} \exp(\Delta H_2/RT) \text{ s}, \quad (9b)$$

with activation energies

$$\Delta H_1 = 9.835 \text{ kJ/mole,}$$

$$\Delta H_2 = 16.750 \text{ kJ/mole.}$$

From (1) the following identity

$$\tau_M = \frac{3}{2} \tau_{C1}, \quad (10a)$$

$$\tau_B = \frac{3}{2} \tau_{C2}, \quad (10b)$$

has to be taken into account and we find that both neutron and NMR results are in agreement.

5. Conclusion. — Using the quasielastic neutron scattering technique, the molecular dynamics of trimethylacetic acid has been investigated in its lower temperature phase. NMR results are confirmed. Determination of the experimental EISF unambiguously proves the existence of 120° reorientations of both methyl and t-butyl groups. Rigorously, experimental spectra would have to be corrected for multiple scattering. However the thickness of the sample was chosen to be as thin as possible in order to reduce these effects, which have been evaluated to be less than 5%. Consequently this does not change our conclusions nor does it introduce noticeable deviations in the obtained values of the correlation times.

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