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Reorientations in pivalic acid (2,2-dimethyl propanoic acid).
II. Incoherent quasielastic neutron scattering study

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Résumé. — Nous avons étudié les mouvements de rotation de l'acide pivalique dans sa phase solide plastique,
en utilisant la spectrométrie de neutrons par temps de vol. L'étude a porté sur quatre échantillons différents par-
tiellement deutériés, afin d'analyser les mouvements respectifs des diverses parties de la molécule. En étudiant
le composé (CH₃)₃CCOOD, nous avons pu extraire un facteur de structure élastique incohérent qui correspond
to un modèle fondé sur une combinaison d'une diffusion rotationnelle uniaxiale des groupements t-butyles autour
de leur axe de symétrie d'ordre trois avec des fluctuations du grand axe des dimères autour de leur direction moyenne
d'orientation le long des axes [110] du réseau. La largeur de la fonction de distribution est d'environ 10°. Une ana-
lyse phénoménologique de la partie basse énergie des spectres inélastiques sur la base d'un oscillateur suramorti
unique confirme ces résultats, en conduisant à une amplitude moyenne de 8° environ. En soustrayant les spectres
obtenus avec le composé complètement deutérié (CD₃)₃CCOOD de ceux mesurés avec (CD₃)₃CCOOH, il est
possible d'étudier le mouvement du groupement carboxylique. Celui-ci consiste en des sauts de 180° autour de
la liaison moléculaire centrale C-C. Tous ces résultats sont en parfait accord avec les mesures effectuées à partir
du composé complètement hydrogéné (CH₃)₃CCOOH.

Abstract. — Rotational motions of pivalic acid are analysed in its solid plastic phase, using time of flight neutron
spectroscopy. Four different partially deuterated compounds are studied, to analyse motions of the different parts
of the molecule. From a study of the compound (CH₃)₃CCOOD, an elastic incoherent structure factor is extracted
which corresponds to a model based upon uniaxial rotational diffusion of the t-butyl groups about their threefold
symmetry axis, together with fluctuations of the long axes of the dimer units, about their mean direction of orien-
tation along the [110] lattice axes. The width of the angular distribution is found equal to about 10°. A pheno-
monological analysis of the low-energy part of the inelastic spectra in terms of a single overdamped oscillator
confirms these results, leading to a mean oscillatory amplitude of about 8°. Subtraction of the spectra obtained
with the fully deuterated compound (CD₃)₃CCOOD, from those measured with (CD₃)₃CCOOH enables the
study of the motion of the carboxylic group. This is found to consist of 180° jumps about the central molecular
C-C bond. These results are entirely consistent with the measurements performed on the fully hydrogenated
compound (CH₃)₃CCOOH.

1. Introduction.

Pivalic acid (CH₃)₃CCOOH formally known as 2,2-dimethyl propanoic acid (also trimethylacetic acid) undergoes a solid-solid phase transition at Tₜ = 279.9 K (ΔSₜ = 7.1 cal mol⁻¹ K⁻¹) and melts at Tₘ = 308.5 K (ΔSₘ = 1.8 cal mol⁻¹ K⁻¹). The low-temperature phase is triclinic [1] whilst the high-
temperature phase is orientationally disordered [2] : the lattice is face-centred-cubic, space group Fm³m with unit cell parameter a = 8.87 ± 0.03 Å and four molecules in the unit cell. Taking into account the
molecular symmetry, such a structure is possible only if the molecules reorient between several equili-

brium positions. Clearly, the central C-C axes of the molecules along either of the <110> directions of
the lattice and the planes of the carboxylic groups seem to coincide with the (100) crystal planes. Depend-
ning on the position of the hydrogen atoms of the methyl groups, two configurations are possible. They are
referred to as LEM or Calder. Moreover, earlier dielectric relaxation measurements [3] have led to
the hypothesis of the existence in the plastic phase of non-polar dimer units, formed by two nearest-
neighbour molecules linked by two hydrogen bonds.

Since 1970, a number of data have been produced concerning the dynamics of this system. The dynam-
ical nature of the disorder is clearly shown by
NMR [4-6]. Characteristic times and activation energies were obtained, corresponding to translational self-diffusion of the molecules and also to reorientations of the whole molecule or of its different parts. Translational self-diffusion was also studied by radio-tracer experiments [7-9]. A comparison of the results obtained by these different techniques is given in the part I of this paper.

This work uses Incoherent Quasielastic Neutron Scattering (I.Q.N.S.) to observe the proton self-correlation function via its space-time Fourier transform, the incoherent scattering function $S_{\text{inc}}(Q, \omega)$. This function contains all the information about the proton single-particle motion, and thus also describes the rotational motion of the molecule and of its parts. Pivalic acid was first studied by I.Q.N.S. in 1977 by Leadbetter and Turnbull [10]. However, poor instrumental resolution prevented them from distinguishing between several possible models for molecular motions. Recently, we have performed another experiment of the low temperature phase [11], which unambiguously proved the existence of simultaneous 120°-reorientations of the methyl and t-butyl groups below 280 K.

Due to the large incoherent scattering cross section of hydrogen ($\sigma_{\text{inc}} = 80$ barns) the main contribution to the scattered intensity arises from the hydrogen atoms in the molecule. By replacing well-defined hydrogen atoms by deuterium ($\sigma_{\text{inc}} = 2$ barns), the motions of the different parts of the molecule can, in principle, be investigated separately.

Our aim in the part II of this paper is to report the experiments that we have performed for the plastic phase of pivalic acid, using four deuterated species: $(\text{CH}_3)_3\text{CCOOH}$ (hereafter referred to as $D_1$), $(\text{CH}_3)_3\text{CCOOH}$ (referred to as $D_2$), $(\text{CD}_3)_3\text{CCOOH}$ and fully deuterated $(\text{CD}_3)_3\text{CCOOH}$ (referred to as $D_4$ and $D_{10}$, respectively). The deuteration of the $D_1$, $D_9$ and $D_{10}$ species was verified by Raman spectroscopy. The H acid was deuterated better than 97%, and the t-butyl was fully deuterated. In part I of this paper, various rotational incoherent neutron scattering laws were derived, corresponding to different combinations of possible motions for methyl, t-butyl, carboxylic group or whole molecule. These laws will be compared with experimental results obtained with each deuterated compound.

2. Experimental equipment and corrections.

I.Q.N.S. experiments were performed at the Institut Laue-Langevin with the time-focussing time-of-flight spectrometer. IN6. Three sets of measurements were performed, using incident wavelengths of $\lambda = 5.9$ Å, 5.1 Å and 4.1 Å, corresponding to energy resolutions (fwhm) of about 70 μeV, 100 μeV and 180 μeV, respectively. In each case, several spectra were recorded simultaneously for neutron momentum transfer $Q$ ranging from $\approx 0.2$ Å$^{-1}$ to 1.8 Å$^{-1}$ ($\lambda = 5.9$ Å), 2.1 Å$^{-1}$ ($\lambda = 5.1$ Å) or 2.5 Å$^{-1}$ ($\lambda = 4.1$ Å).

The powder specimens of pivalic acid were held in a slab-shaped aluminium container with a diameter of 50 mm and a thickness of 0.3 mm. When perpendicular to the beam, they transmitted about 92 per cent of the incoming neutrons. All the experiments were carried out in transmission geometry using an angle of 135° between the plane of the samples and the incident neutron beam.

Pivalic acid was studied in its plastic phase at $T = 303$, 290.5 and 283 K. Measurements were also performed at $T = 278$ K in both the supercooled plastic phase and the low-temperature phase.

The neutron raw-data were corrected for detector efficiency, sample holder scattering, absorption and self shielding and then transformed into energy scale. For each sample, data collected at the same temperature with the same value of the incoming neutron energy were compared by a least square fit to the following scattering function

$$S_{\text{inc}}(Q, \omega) = \exp(-2W)S_{\text{inc}}^1(Q, \omega) + S_{\text{inc}}^0(Q, \omega)$$

folded with the instrument resolution function. In this expression $S_{\text{inc}}^0(Q, \omega)$ is the rotational scattering function corresponding to the assumed model (see paper I). The Debye-Waller factor $\exp(-2W)$ describes the attenuation effect caused by periodic lattice motions. $S_{\text{inc}}^1(Q, \omega)$ is an inelastic term, which can be considered as a slowly varying function of energy. Usually, this term contributes very little to the scattering in the quasielastic region and can be taken into account by a one phonon expansion [12]. The multiple scattering contribution was not taken into account. Indeed, these effects were evaluated from a semi-analytical calculation [13, 14] to be less than 4% of the total.

We shall now analyze the results obtained with each of the partially deuterated compounds.

3. $D_1$ compound.

Using the partially deuterated $D_1$ compound, only the motions of the t-butyl are « visible », i.e. the quasi-totality of the observed intensity (outside the Bragg peaks) is due to the incoherent scattering from the hydrogen atoms belonging to the t-butyl group. These atoms are involved into three kinds of motion:

i) rotation of the methyl groups about their own threefold axis

ii) rotation of the t-butyl about the central C-C bond of the molecule

iii) whole-molecule tumbling.

However, only the reorientations which occur with a jump-rate compatible with the time scale accessible to the spectrometer will be responsible for the quasielastic broadening in the experimental spectra.

Typical examples of time-of-flight spectra, obtained
with one incident wavelength, are shown in figure 1.
They correspond to the same temperature $T = 303 \text{ K}$ and they are displayed as function of the scattering angle $2 \theta$. Clearly, two remarks are noteworthy. First, a sharp elastic component tells us that the motions are essentially local and probably consist of rotations. They appear to be very fast as indicated by the large quasielastic intensity which is underlying the elastic line. The intensity of this elastic line strongly decreases with $Q$, indicating that the portion of space accessible to an individual scatterer (proton) on the experiment time-scale is rather large. The second important point is that the quasielastic and the inelastic part of the spectra are not well separated from each other. Furthermore, a graphical extrapolation towards the elastic region of the scattered intensity originating from lattice vibrations, while imprecise, leads to a significant contribution in the quasielastic range.

Fig. 1. — IN6 time-of-flight spectra of pivalic acid in its plastic phase ($T = 303 \text{ K}$), for different values of the scattering angle. The incident wavelength is $\lambda = 5.1 \text{ Å}$.

3.1 Determination of the Experimental EISF. — To obtain more precise information about the nature of the molecular motions, the spectra, transformed into energy-scale, are usually analysed in terms of their purely elastic, $I_{el}$, and quasielastic, $I_{q}$, parts. For each value of the momentum transfer $Q$, the « experimental » Elastic Incoherent Structure Factor (EISF) is defined as the ratio $I_{el}(Q)/(I_{el}(Q) + I_{q}(Q))$. It gives a direct measure of the time-averaged spatial distribution of the protons and hence information about the rotational trajectories of the molecules. Therefore, it enables to conclude what types of motions are sufficiently fast to be resolved from the elastic peak and to propose a physical model to be compared with the observed quasielastic spectra.

Determination of an experimental EISF by graphically separating the elastic part of the observed spectra is rather imprecise. Indeed, spectra are recorded at constant scattering angle $2 \theta$, and therefore, the value of the momentum transfer $Q$ varies inside the spectrum, as function of the energy-exchange $\hbar \omega$. That is especially true in our case, where the broadening is very important and integration has to be taken up to large values of $\hbar \omega$. Moreover, when converted into energy-scale the maximum in the inelastic region disappears and the separation of the intensity into $S^{R}(Q, \omega)$ and $S^{I}(Q, \omega)$ is not easy.

3.1.1 The EISF-determination procedure. — Use can be made of a systematic method based upon a non-linear least-square fitting procedure [12, 15]. The advantages of this technique have been already discussed [16] and we shall recall only its main features here. This method is based upon the fact that the rotational incoherent scattering law for any bounded-motion model can be separated formally into a purely elastic, $A_{0}(Q) \delta(\omega)$, and a quasielastic, $S^{R}(Q, \omega)$, components

$$S^{R}(Q, \omega) = A_{0}(Q) \delta(\omega) + S^{R}(Q, \omega). \quad (2)$$

The width of the quasielastic part $S^{R}(Q, \omega)$ is an adjustable parameter to be refined to the experimental data. Therefore, the main difference between the real spectrum and a spectrum predicted by any model lies in the intensity of the elastic peak, which depends on the trajectories accessible to one individual proton. Taking for $A_{0}(Q)$ and $S^{R}(Q, \omega)$ expressions corresponding to a known scattering law, e.g. as indicated in part I, the experimental spectra are simulated by a law of the form [15, 16]:

$$S_{fit}^{R}(Q, \omega) = f(Q) A_{0}(Q) \delta(\omega) +$$

$$+ \frac{1-f(Q) A_{0}(Q)}{1-A_{0}(Q)} S^{R}(Q, \omega). \quad (3)$$

For each spectrum, the significant parameters of the fit are $f(Q)$ and the relevant jump-rate probabilities for a proton involved in the model under test. The weight parameter $f(Q)$ controls the amount of elastic intensity for each spectrum. Then, even if the theoretical model does not correctly describe the dynamics of the motion, it is expected that the product $f(Q) \times A_{0}(Q)$ tends, nevertheless, to the correct (experimental) EISF. It can be seen in figure 2 that the models based on 120° or 60° jumps of methyl groups alone (models $M_{3}$ and $M_{6}$, respectively) predict an important amount of elastic intensity, at least while $Q \leq 1.5 \text{ Å}^{-1}$.

Clearly, these models do not correspond to the experimental data which are illustrated in figure 1 and we can conclude that 120° or 60° reorientations of the methyl groups, if they exist (on the instrument time-scale), certainly do not occur alone. Conversely, in the $Q$-range from 1.4 to 2.0 $\text{ Å}^{-1}$, the purely elastic contribution, whilst small, never disappears completely, and tumbling of monomers or dimers as a whole can be excluded. Then we are dealing with models which predict a variation of the EISF as function of $Q$ inter-
3.1.2 Result analysis and comparison with models. — Values of the experimental EISF $f(Q) A_0(Q)$ are reported in figure 2, for the three incident wavelengths and at the different temperatures of analysis. It turns out that the model based upon 60° jumps reorientations of t-butyl groups alone, agrees fairly well with the experimental data. In this model the methyl are fixed, in the configuration referred as LEM in paper I. On the other hand, models based upon methyl-reorientations alone, or involving a whole-molecule tumbling are inaccurate to describe the data.

Deviation of experimental EISF values from the curves predicted by models involving simultaneous reorientations of t-butyl and methyl groups tend to discard these models. Nevertheless, the possibility of a description based upon two types of motions cannot be radically excluded:

(i) Experimental values of the EISF were determined, for each momentum transfer $Q$, from a series of refinement, in which the initial values, the range of energy-transfer, etc. were different. Values reported in figure 2 can be considered as stable with regard to the fit-conditions. The values obtained with the incident wavelength $\lambda = 5.9 \text{ Å}$ lie systematically slightly below the theoretical curve, for the two temperatures of experiment. Thus the use of different instrument resolutions (fwhm 0.076 meV, 0.098 meV and 0.200 meV with $\lambda = 5.9 \text{ Å}, 5.1 \text{ Å}$ and 4.1 Å, respectively), can reveal different aspect of the scattering function.

(ii) The separation between elastic, quasielastic and inelastic contributions, obtained from refinements, is illustrated in figure 3. Clearly, the contribu-
The influence of the vibrational term is rather large, and it should be confirmed that the Lorentzian function introduced to describe \( S(Q, \omega) \) in fact does not take a part of the quasielastic intensity into account.

Another experimental EISF was calculated, for each value of the momentum transfer, including the «inelastic» intensity in the quasielastic term.

\[
A_0^{\text{exp}}(Q) = \frac{f(Q) A_0(Q)}{A + A_1(Q)}.
\]

These values are reported in figure 4. Resulting values fall in the range of the amount of elastic intensity predicted by the \( B_3 \otimes M_6 \) or \( B_6 \otimes M_3 \) models. But large discrepancies clearly occur in the \( Q \) range varying from 1.0 to 1.7 Å\(^{-1}\), which cannot be explained by arguing from the existence of two strong Bragg peaks at \( Q = 1.23 \) Å\(^{-1}\) and \( Q = 1.42 \) Å\(^{-1}\).

![Fig. 4. — Experimental EISF values obtained when including the inelastic intensity into the quasielastic term (Eq. (5)). These are compared with theoretical variations for models based on different combinations of simultaneous reorientations of methyl and t-butyl groups. Bragg peak positions are indicated by arrows. Notations and symbols as in figure 2.](image)

Nevertheless, to conclude on this hypothesis of the simultaneous occurrence of methyl and t-butyl reorientations, a series of refinements of (1) based on the \( B_3 \otimes M_6 \) model, was carried out. The inelastic contribution was taken into account by a flat background.

The values of the EISF theoretically predicted could be extracted from the spectra, but providing that the range of energy-transfer over which the data were analysed, was drastically restricted (\( \pm 3 \) meV). Above all, outside this range, the scattering law evaluated from the final values of the fit-parameters strongly deviated from the experimental data, which were found to lie systematically below the predicted theoretical values. None of the others models allowing for methyl and t-butyl jumps was found able to correctly describe the data over a large (\( -4 \) meV-10 meV) energy range. Finally another fact tends to bring discredit on these models. Starting from any initial value all the refinements led to a characteristic time associated to the reorientations of the methyl groups of the order of \( 0.3 \times 10^{-12} \) s, and depending on the amplitude of the background accounting for the inelastic contribution. Then the Lorentzian functions in the scattering law whose widths involve methyl jump-rates were found to correspond to the widest part of the spectra, exactly as the single Lorentzian function \( L(t, \omega) \) in the first analysis. But their weight in the total scattering law is imposed by the quasielastic structure factors of the model, contrarily to the amplitude \( A_1(Q) \) which was allowed to vary. Then they are unable to take into account fully the widely-broadened part of the spectra. Therefore the flat background parameter increases meaningless, predicting a scattered intensity outside the analysis range larger than that observed. On the other hand, refined values of the correlation times associated to t-butyl reorientations were found in accordance with those previously obtained. Furthermore, it is noteworthy that a value of \( \tau_{\text{eq}} \approx 0.3 \times 10^{-12} \) s is inconsistent with the conclusions of the analysis of the inelastic part of the spectra, as it will be shown in section 3.2, and also of other neutron and NMR studies of similar t-butyl compounds. This point will be discussed in the conclusion of this paper.

### 3.1.3 The influence of molecule oscillations.

Taking as reasonable conclusion that only reorientations of the t-butyl groups are visible on the instrument time-scale, the origin of the broad component underlying the spectra has to be elucidated. In fact, in the plastic phase, dimeric units of pivalic acid molecules are elongated in shape. Therefore, another model, intermediate between the tumbling model and the model based on uniaxial reorientations about the molecule long axis can be imagined. In this model, in addition to rotation about the molecule axis, the molecular motion also comprises rapid fluctuations of this axis about its equilibrium position. This model was developed in connection with molecular motions in liquid crystals [15, 17, 18]. The full incoherent scattering law is difficult to calculate but the corresponding EISF is easily obtained (see part I, eqs. (15) and (18)). The comparison of the experimental EISF together with the theoretical EISF of this model for various values of the mean amplitude \( \Delta x \) of the fluctuations of the dimer axis is illustrated in figure 5. It is seen that this model agrees well with the experimental data, with a value of \( \Delta x \) of about 10°.

It must be pointed out that the central ring of a dimer unit which is formed by two carboxylic groups linked by two hydrogen bonds, is not rigid. As a consequence of this ring deformation, the t-butyl groups will perform large amplitude oscillations with respect to each other. However, when concerned with incoherent neutron scattering, we look at each
Fig. 5. - Experimental EISF values obtained when including the inelastic intensity into the quasielastic term (Eq. (5)). These are compared with theoretical variations as a function of $Q$ predicted by a model based upon an uniaxial rotation of the t-butyl with simultaneously rapid fluctuations of the dimer axes. Four curves are illustrated, corresponding to several widths of the angular distribution of these fluctuations. Vertical arrows denote the Bragg peak positions. Notations and symbols as in figure 2.

proton individually. Therefore, as in this complex motion each part of the molecule oscillates about the centre of mass of the dimer unit, which is located in the middle of the central ring, the corresponding EISF is exactly the same as for whole dimer oscillations, with the central ring assumed to be rigid.

To summarize this analysis, the extraction of an experimental EISF from the ratio of the purely elastic intensity over the total intensity, in an energy-transfer range up to 10 meV, permits to conclude that, on the $10^{-11}$-10$^{-13}$ s time scale, large amplitude overdamped oscillations exist, which can be attributed, either to the whole-dimer, or also to oscillations of the t-butyl groups, with a deformation of the central ring. Simultaneously, uniform rotation of the protons of the t-butyl groups occur, about the molecule long axis, which can result, either from rotation of the whole dimer, or from individual rotations of each t-butyl group. Rotations of methyl groups appear too slow to be visible on the instrument time-scale. Nevertheless, data obtained at 30.5 °C, with the best instrument resolution ($\lambda = 5.9$ Å), lead to experimental values of the EISF below the theoretical curves in figures 2, 4 and 5. Therefore, at this temperature, the motion of the methyl groups is perhaps just at the limit to be resolved on this instrument time-scale. More information about the dynamics of the methyl groups can be obtained from the analysis of the inelastic part of the spectra.

3.2 ANALYSIS OF THE INELASTIC PART OF THE SPECTRA.
— Pivalic acid was extensively studied using Raman scattering [19, 20]. A normal coordinate treatment was performed for the four isotopes $D_0$, $D_1$, $D_9$ and $D_{10}$ [20], in terms of independent force constants. The

good agreement with the experiment provides a detailed description of the intramolecular motions, especially in the low-frequency region. Particularly, torsional oscillations are found in that range. The analysis of the corresponding force constants provides information about the heights of the maxima of the hindering potential for both methyl and t-butyl. As these motions correspond to rather large amplitude of oscillation, they should be visible in a neutron inelastic scattering experiment.

Variations of the usual function [21] :

$$P(\alpha, \beta) = \frac{\omega^2}{Q^2} S(Q, \omega)$$

where $\alpha = \frac{\hbar^2 Q^2}{2 k_B T}$ and $\beta = \frac{\hbar \omega}{k_B T}$ as function of the energy transfer $\hbar \omega$, are shown in figure 6, for different values of the scattering angle, in both the low-temperature and plastic phases. Due to the temperature of the experiment, spectra were obtained in up-scattering, using an incident wavelength of neutrons $\lambda = 4.1$ Å corresponding to an initial energy $E_0 \approx 4.9$ meV.

Fig. 6a. — Experimental values of the function $P(\alpha, \beta)$ in the low temperature phase of $D_1$ pivalic acid ($T = 253$ K), as a function of the energy transfer, for three scattering angles.

Only the region $0 < \hbar \omega < 80$ meV is shown. At higher values of the energy transfer, the instrument resolution becomes rapidly very poor. Furthermore, multiphonon processes become important. Consequently the spectra very quickly lose all structure beyond 40 meV.

In the range 20-40 meV (160-320 cm$^{-1}$), a pro-
Fig. 6b. — Experimental values of the functions $P(\alpha, \beta)$ in the plastic phase of $D_1$ pivalic acid ($T = 303$ K) as a function of the energy transfer for three scattering angles.

Fig. 7. — Experimental values of the functions $P(\alpha, \beta)$ in the plastic phase of fully deuterated pivalic acid $D_{10}$ ($T = 283$ K), as a function of the energy transfer, for several scattering angles.

nounced wide band appears, composed of several, not resolved peaks. Referring to the results of the Raman analysis, contributions of the torsion of methyl groups should be expected at 256 and 263 cm$^{-1}$, but also deformations $\delta_{\text{CC}}$ of the system $\text{C}-\text{C}-\text{C}$ at 248 cm$^{-1}$ and vibrations at 287 cm$^{-1}$ involving methyl torsions and rotations of the $\text{C}-\text{C}_3$ group.

It would be worth to follow the methyl-torsion frequencies as function of temperature to determine whether any change in their dynamics occurs at the phase transition.

For the reasons previously indicated (i.e. the poor instrument resolution in that range and the multiphonon cross-section), this is extremely difficult. Few remarks can be made, except that in the plastic phase, the band is still less structured and that the shoulder at 203 cm$^{-1}$ disappears. This peak at 203 cm$^{-1}$ is not mentioned in the Raman study [20], for measurements performed near the transition temperature. But at the liquid nitrogen temperature, a weak line appears [22, 23]. Similarly, inelastic neutron scattering experiments at $T = 20$ K, evidence a well-defined peak at 202 cm$^{-1}$ and, in the same time, a strong peak at 256 cm$^{-1}$ which can be attributed to the methyl torsion.

Conversely, in the range 0-20 meV (160 cm$^{-1}$), the changes at the phase transition are more important. In the low temperature phase, the functions $P(\alpha, \beta)$ reveals four peaks at 37, 55, 91 and 130 cm$^{-1}$, also well observed by low temperature Raman spectroscopy [22]. According to the conclusions of the Raman study, the line at 130 cm$^{-1}$ corresponds to the stretching of the hydrogen bonds $v_{\text{OH}}-\cdot-\cdot\cdot\text{O}(\text{Ag})$ in which the two parts of the dimer move with respect to each other. While the vibration $v_{\text{OH}}-\cdot-\cdot\cdot\text{O}(\text{Bu})$, predicted at 107 cm$^{-1}$ is not visible, the peak at 55 cm$^{-1}$ can be attributed to the mode $\beta_{\text{O}}-\cdot-\cdot\cdot\text{O}$ which was also observed at 59 and 56 cm$^{-1}$ using IR and Raman spectroscopy [22, 23]. At 91 cm$^{-1}$ appears a torsional mode of the $\text{C}-\text{C}$ bond between the carboxylic group and the $t$-butyl group. This torsion is also involved in the line at 37 cm$^{-1}$ where it is coupled to a deformation of the carboxylic ring ($t_{\text{OH}}-\cdot-\cdot\cdot\text{O}$).

Above the phase transition, the peaks disappear. The general shape is that of a single broad band. Furthermore, the maximum of this part of the spectrum is shifted towards the low frequencies. Simultaneously the shape of the spectrum in the vicinity of $\hbar\omega = 0$ noticeably changes. In the low temperature phases the spectrum increases form zero as function of $\omega^2$, while the increase is linear in the plastic phase.

In the low frequency region, the spectrum is not the simple superposition of a series of internal vibrations of the pivalic molecule. In figure 7 the inelastic spectrum obtained with the fully deuterated isotope $D_{10}$ is illustrated. The intensity in the region 100-320 cm$^{-1}$ is strongly reduced. However, some structures are still visible. At about 118 cm$^{-1}$, a small peak corresponds to the $v_{\text{OD}}-\cdot-\cdot\cdot\text{O}$ mode. The methyl torsions

\begin{itemize}
  \item At 248 cm$^{-1}$, deformations $\delta_{\text{CC}}$ of the system $\text{C}-\text{C}-\text{C}$
  \item At 287 cm$^{-1}$, involving methyl torsions and rotations of the $\text{C}-\text{C}_3$ group.
\end{itemize}
are shifted from 256 cm\(^{-1}\) to 185 cm\(^{-1}\), comparatively to the D\(_0\) compound. Vibrations \(\delta_{\text{CC}}\) and rotations of the CC\(_3\) groups should suffer only small change and can be supposed to correspond to the region 245-300 cm\(^{-1}\).

At low frequency, a sharp peak is visible, whose intensity strongly decreases as function of the scattering angle. This can be attributed to the external vibrations. A qualitative description of the behaviour of the spectrum near \(\hbar \omega = 0\) at the phase transition can be given as follows. Calculation of molecular dimensions from atomic coordinates show that the dimer units are elongated, with a general dumbbell shape. Therefore two types of motions have been considered in the EISF analysis, i.e. rotations about the long axis and fluctuations of this axis.

In the low temperature phase, the molecules are, most of the time, trapped in the minima of the potential (with sometimes reorientations of the t-butyl group) where they undergo almost undamped oscillations. Above the phase transition, the dynamics changes drastically. First, reorientations of the t-butyl groups occur on a more rapid time scale and then, librations of the long axis become overdamped. The passage from an oscillatory regime to a diffusive regime manifests itself by a change in the shape of \(P(\alpha, \beta)\) near \(\hbar \omega = 0\) and an increase of the intensity in the quasielastic region. To confirm this hypothesis, a phenomenological analysis of the low frequency vibrations was performed.

3.3 PHENOMENOLOGICAL APPROACH. — The spectra \(P(\alpha, \beta)\) obtained in the plastic phase at each scattering angle were analysed in terms of a single overdamped oscillator, in the range \(\hbar \omega < 20\) meV. This enables to obtain for each angle a value of the frequency \(\omega_0\) and of the damping constant \(\gamma\). Values obtained with the three incident energies were found to coincide perfectly, as illustrated in figure 8. The values of the frequency are found to follow a linear variation as function of the square of the momentum transfer, except at small-\(Q\) values. From these experimentally determined values, it was then possible to evaluate the contribution of the scattering function \(S^1(Q, \omega)\) in the quasielastic part of the spectra.

In paper I, the scattering law for a damped harmonic oscillator was derived:

\[
S(Q, \omega) = \exp\left(-Q^2 \left\langle u^2 \right\rangle \right) \times \\
\times \left[ \delta(\omega) + \frac{Q^2}{\hbar \omega} \frac{\left\langle u^2 \right\rangle}{\pi} \frac{\omega_0 \gamma}{\exp\left(\frac{\hbar \omega}{k_B T} - 1\right)} \right].
\]

Here \(k_B\) is the Boltzmann constant, \(\left\langle u^2 \right\rangle\) is the mean square amplitude of the displacement of the scatterer in the oscillatory motion. It is related to the mean square angular libration of the molecule \(\left\langle \theta^2 \right\rangle\) by:

\[
\left\langle u^2 \right\rangle = \frac{I}{M} \left\langle \theta^2 \right\rangle
\]

where \(I\) and \(M\) are the moment of inertia and the mass of the molecule respectively. When folded with the rotational function \(S^R(Q, \omega)\), the first term in the brackets leads to the quasielastic intensity, whilst the second, which is slowly varying with energy, is nearly unaffected, and gives rise to inelastic scattering. Furthermore \(\left\langle u^2 \right\rangle\) controls the amount of inelastic scattering, as a function of \(Q\):

\[
\frac{I^\text{inel}(Q)}{I^\text{quasi}(Q) + I^\text{inel}(Q)} \approx \frac{Q^2 \left\langle u^2 \right\rangle}{1 + Q^2 \left\langle u^2 \right\rangle} \approx 1 - \exp\left(-Q^2 \left\langle u^2 \right\rangle\right).
\]

The second equality holds because, in deriving (7), we restricted to a one phonon expansion (see part I).

The expression (7) was introduced into (3), folded with the instrument resolution and refined to the experimental data, for D\(_1\) compound. The phenomenological values obtained at each scattering angle for \(\omega_0\) and \(\gamma\) were introduced as parameters and kept constant in the refinements.

Spectra were analysed in the range \((-4\,\text{meV}, +10\,\text{meV})\). As in the plastic phase, the inelastic peaks originating from torsions of the t-butyl groups disappear from the spectra, the rotation of these groups was more conveniently described in terms of a uniaxial diffusion about their axes than in terms of \(60^\circ\) jumps. Indeed, whilst these two models lead to practically the same EISF in the instrument range, the quasielastic part of their respective scattering law involve contributions of Lorentzian functions whose widths largely differ (see part I). Since spectra are recorded at constant angles, at large energy transfer values, the momentum transfer \(Q\) differs significantly from its value at \(\hbar \omega = 0\). The uniaxial diffusion model pro-

![Fig. 8. — Frequency \(\omega_0\) of the overdamped oscillator in the phenomenological description of the low-frequency inelastic part of the spectra, obtained from refinements to experimental data and plotted as a function of the square of the momentum transfer, \(Q^2\).](image-url)
vides broad quasielastic contributions for this high-$Q$ range, whilst the widest width predicted by the $60^\circ$ jump model is $2/\tau_b$, and the intensity of the corresponding Lorentzian function is negligible at large $h\omega$ values. In fact the $60^\circ$ jump model also predicts torsional modes of the t-butyl groups in the minima of the potential. If these modes are strongly damped, as suggested by the absence of structure in the inelastic scattering, they have a diffusive behaviour, yielding to intensity in the quasielastic region. For all these reasons, the uniaxial diffusion model appears more convenient to describe the data. The fit parameters 

$$
\langle u \rangle^2 = \left( \frac{1}{3} R_1 + \frac{2}{3} R_2 \right)^2 \langle \theta^2 \rangle
$$

(10)

where $R_1 = 5.21 \text{ Å}$ and $R_2 = 4.18 \text{ Å}$ are the two possible distances for a methyl hydrogen atom with respect to the centre of gravity of the dimer. The mean angular amplitude of oscillation $\langle \theta \rangle = \sqrt{\langle \theta^2 \rangle} \approx 8^\circ$ derived from (6) is in agreement with the value $\Delta\theta \approx 10^\circ$ obtained in section 2. Furthermore, in figure 10, we have reported the ratio of the scattered intensity originating from librations over the total scattered intensity, as obtained from the separation based upon a single Lorentzian (see Eq. (4)). The full line is the variation evaluated from (7) using the value $\langle u^2 \rangle = 0.42 \text{ Å}^2$. Acceptable agreement is found, for data obtained at $\lambda = 5.9 \text{ Å}$ and $5.1 \text{ Å}$ ($Q \approx 2 \text{ Å}^{-1}$), taking into account that the separation based on (4) is rather imprecise at low $Q$ values and that a single lorentzian hardly takes into account the full inelastic intensity at large $Q$ where multiple phonons also contribute. Deviations are important for largest $Q$-values ($\lambda = 4.1 \text{ Å}$).

Finally, the data obtained at $T = 30.5 \text{ °C}$, with the incident wavelength of neutrons $\lambda = 5.9 \text{ Å}$, were refined on the basis of this model, but introducing the quasielastic scattering law based on simultaneous occurrence of reorientation of t-butyl and methyl groups. These were allowed to perform $120^\circ$ jumps about their threefold axis, like in the low-temperature phase. This assumption was supported by the fact
that in the inelastic part of the spectra, the torsional vibrations of methyl groups were still visible in the plastic phase, especially with the D\textsubscript{10} compound. Therefore the potential acting on these groups appears essentially intramolecular in nature and no major modifications should occur at the transition. In fact, due to the Q-range accessible, the distinction between 120° and 60° jumps of the CH\textsubscript{3} groups is rather arbitrary. The correlation time for the t-butyl groups was kept fixed at the value obtained from refinements of data obtained at 5.1 Å and 4.1 Å. A final value for t\textsubscript{M3}, was found equal to (1.03 ± 0.5) \times 10^{-10} s in agreement with the value extrapolated at this temperature from the Arrhenius law in the low-temperature phase. However, this value is much smaller than the instrument resolution and the uncertainty of its determination is large. The smaller EISF values obtained with \( \lambda = 5.9 \) Å can result from some artefact and the apparent agreement for the t\textsubscript{M3} value can be quite fortuitous. Therefore, no precise conclusion can be drawn from this result except that it confirms the absence of drastic change in the dynamical behaviour of the methyl at the transition.

In conclusion, on the IN6 time-scale, the molecular motions in pivalic acid, as obtained from the analysis of the D\textsubscript{1} compound (i.e., without any information on the dynamics of the carboxylic group) can be described as follows:

(i) The methyl groups experience a strong intramolecular hindering potential. No change occurs in their dynamics at the phase transition from the low-temperature phase. Their motion is too slow to be visible on the IN6 time-scale, except at 30.5°C, using the best instrument resolution (with \( \lambda = 5.9 \) Å).

(ii) The t-butyl groups undergo rapid reorientations about their threefold symmetry axes. In the Q-range accessible to the instrument, this motion can be described as 60° jumps rotations (from the analysis of the EISF). However, if the range of energy transfer under consideration is largely extended, in the wings of the spectra at constant angle the momentum transfer Q goes beyond the limit Q, \( \leq \pi \). Thus the motion is more likely described in terms of a uniaxial diffusion. An explanation is that the librations of the t-butyl groups in the minima of the sixfold potential are damped and more likely exhibit a diffusive, rather than an oscillatory, behaviour.

Making use of the usual relation (see part I, Eq. (9)),

\[
D_r = \frac{1}{2} \tau_{R_6}
\]

the results of the refinements at different temperatures, using different incident neutron wavelengths are reported in figure 17. They can be described by the unique following relation:

\[
\tau_{R_6}(s) = (3 ± 0.7) \times 10^{-14} \exp(\Delta H_\text{b}/RT)
\]

with \( \Delta H_\text{b} \) equal to 12 ± 2 kJ mol\(^{-1}\).

(iii) In the same time, whole-dimer units undergo large oscillatory motions. A first description in terms of diffusive fluctuations of the molecule long axis leads to a mean value of the width of the angular distribution of about 10°. A second analysis, based upon a damped oscillatory motion of the long axis, yields to overdamped librations, whose average value is about 8°, in accordance with the first description. These values are small in comparison with the angle of 60° between two adjacent [110] equilibrium directions of the molecule axis. Therefore no tumbling motion is visible in the IN6 range.

4. D\textsubscript{9} and D\textsubscript{10} compounds.

With the D\textsubscript{9} compound, the scattered intensity is essentially incoherent and mainly occurs from the unique proton of the carboxylic group. Referring to part I, this atom is involved in the following motions:

i) rotation of the carboxylic group about the central C-C bond of the molecule

ii) whole molecule tumbling

iii) exchange mechanism in double well potential of the hydrogen bond.

However, while the carbon and oxygen atoms of the molecule have a negligible incoherent cross-section, the incoherent cross-section for the nine deuterium atoms is about 18 barns, to be compared to \( \sigma \approx 80 \) barns for the unique hydrogen. Then the scattered intensity will also reflect the motion of the t-butyl group.

In principle, the relevant correlation times for this motion have been obtained with the D\textsubscript{1} compound, and could be introduced into the scattering law. But the question would arise whether the dynamics of the motion are strictly the same for a protonated and a deuterated t-butyl group. However, a more serious problem occurs due to the coherent scattering from deuterium, carbon and oxygen atoms, whose coherent scattering cross sections are 5.6, 5.6 and 4.2 barns, respectively.

Evaluation of the coherent scattering law requires evaluation of correlation functions:

\[
\langle \exp(iQ \cdot R_i(t)) \exp(-iQ \cdot R_j(0)) \rangle
\]

in which the instantaneous positions \( R_i \) and \( R_j \) of two different atoms \( i \) and \( j \) are involved. Depending upon whether these atoms belong to the same molecule or to two different molecules, the evaluation of these correlation functions leads to the knowledge of orientational correlation functions for one or two molecules. In the first case, calculations are analogous to those required for the incoherent scattering law. But in the second case, they become rapidly intractable without drastic approximations.

Another method is to perform a « background » experiment with the fully deuterated compound D\textsubscript{10} and to subtract the scattered intensity from the spectra obtained with D\textsubscript{9}. Indeed, the incoherent scatter-
ing occurring from the t-butyl is the same in both experiments and it can be expected that changing one hydrogen for one deuterium in the molecule does not affect greatly the coherent part of the scattering. The resulting spectra \(D_{9}D_{10}\) thus reflect the motion of the acid hydrogen atom alone.

This method was chosen. Great care was taken to make the two specimens \(D_{9}\) and \(D_{10}\) as similar as possible: same thickness, same mass, same compression of the powder in the container. Usual corrections of raw data were applied to \(D_{9}\) and \(D_{10}\) results separately and the two corresponding scattered intensities \(S^{9}(\theta, \omega)\) and \(S^{10}(\theta, \omega)\) were obtained. Then the relevant scattering for the unique acid hydrogen \(S^{H}_{\text{inc}}(\theta, \omega)\) was obtained from:

\[
S^{H}_{\text{inc}}(\theta, \omega) = \frac{S^{9}(\theta, \omega)}{m_{9}} - \frac{S^{10}(\theta, \omega)}{m_{10}} \tag{11}
\]

where \(m_{9}\) and \(m_{10}\) denote the exact mass of \(D_{9}\) and \(D_{10}\) in the neutron beam.

Spectra recorded by the time-of-flight technique were obtained at constant angle \(\theta\). So, inside a spectrum, the momentum transfer \(Q\) depends on the energy transfer \(\hbar\omega\). Consequently, when integrating over all the values of the energy transfer, the integral

\[
I(Q_{0}) = \int_{-E_{0}}^{E_{0}} S^{H}_{\text{inc}}(\theta, \omega) \, d\omega \tag{12}
\]

where \(Q_{0} = Q(\theta, \omega = 0)\) is the \(Q\)-value for \(\omega = 0\) and \(E_{0}\) is the neutron incident energy, does not exactly coincide with the Debye-Waller term \(\exp(-2W)\) obtained when integrating (1) (the inelastic term \(S^{H}_{\text{inc}}(Q, \omega)\) is assumed small enough to be neglected).

Nevertheless, the variation of \(I(Q_{0})\) as a function of \(Q_{0}\) must be monotonous and above all, must be identical whatever value of incident wavelength was used. Figure 11 shows the variation of \(I(Q_{0})\) versus \(Q_{0}\), for each of the three experimental wavelengths. The fact that the three curves are perfectly superimposed proves the validity of our subtraction (11). A deviation from the \(\exp(-2W)\) law appears in the low \(Q\) range, which can be related to the strong low frequency peak in the inelastic spectra \(P(\alpha, \beta)\) which was already mentioned. Since coherent effects mainly predominate at low \(Q\), differences in the scattering between \(D_{9}\) and \(D_{10}\) can affect the result of the subtraction of the scattered intensities. Furthermore the isotopic substitution modifies the strength of the hydrogen bond in the carboxylic ring. Therefore librational oscillations of the two parts of a dimer unit occurring from ring deformations can also be slightly affected. These small effects cannot be clearly evidenced in the \(P(\alpha, \beta)\) representation, but can modify the scattered intensity in the wings of the \(S(Q, \omega)\) spectra.

Typical spectra are shown in figure 12. Unfortunately, the experiments could be performed at one temperature only \((T = 283\, K)\) because they required a long measuring time (small incoherent cross section) in order to keep a good statistics after the subtraction was made.

![Fig. 11. Variation as function of the momentum transfer \(Q_{0} = Q(\theta, \omega = 0)\), of the energy-integral of the spectra obtained by subtracting the \(D_{10}\) spectra from the corresponding \(D_{9}\) spectra, according to (11). Squares, triangles and circles correspond to \(\lambda = 5.9\, A, 5.1\, A\) and \(4.1\, A\), respectively. Vertical arrows indicate the positions of the Bragg peaks.](image1)

![Fig. 12. Quasielastic neutron scattering spectra obtained after subtracting the spectra measured with the \(D_{10}\) compound from the corresponding spectra recorded with the \(D_{9}\) compound. The temperature is 283 K. Two sets of spectra are shown for the wavelengths \(\lambda = 5.9\, A\) and \(\lambda = 5.1\, A\). The full line is the result of the refinement of the model based upon 180° jumps of the carboxylic group. The dotted line is the elastic separation obtained by refinement.](image2)
One notices immediately the large amount of purely elastic scattering, even at large $Q$ values. This tells us that the number of equilibrium positions accessible to the acid proton is rather small. On the other hand, the quasielastic broadening is well in the instrument range. An experimental EISF was extracted, introducing in (3) a model based upon $180^\circ$ rotations of the carboxylic group (see Part I, Table I).

To avoid possible uncertainties occurring from the inelastic contribution, the energy analysis range was restricted to $\pm 1$ meV and a flat background was introduced as refinement parameter. Separation of the elastic part is illustrated in figure 12. The resulting values are shown in figure 13 for the three wavelengths used in the experiment. Clearly, these values fully agree with a model allowing for $180^\circ$ jumps of the carboxylic group. Model assuming jumps over 4 sites or more (i.e. rotational diffusion) can be ruled out as predicting an elastic intensity considerably smaller than observed. This also holds for a $120^\circ$ jump model, whilst this case has not to be considered for symmetry reasons. As already known from the D$_1$-study, the tumbling motion appears to be much too slow to be visible using IN6.

Similarly, the double-well potential model can also be excluded, because it predicts a purely elastic scattered intensity larger than the experimentally observed. This does not rule out the proton exchange mechanism but, if this motion exists, it occurs on a slower time scale, outside the instrument range. It is noteworthy that Meier et al. [24] observed this mechanism in p-toluic acid on the backscattering spectrometer IN13 of the Institut Laue-Langevin, whose instrument resolution is better than the IN6 one and from data recorded over a larger $Q$-range ($Q \leq 4$ Å$^{-1}$). Eventually, since the EISF values obtained with $\lambda = 5.9$ Å lies under the others, it could be assumed that both the proton exchange mechanism and $180^\circ$ reorientations simultaneously occurs, in accordance with the value of about 48 $\mu$eV found by Meier et al. for the hwhm. Actually, considering the IN6 $Q$-range and also the resulting statistics of experimental data after the subtraction $D_0-D_{10}$, no precise conclusion can be drawn on the existence or not of a proton exchange in pivalic dimer.

When fitting all spectra simultaneously, recorded with the same incident wavelength, the following value of the correlation time for $180^\circ$ jumps of the carboxylic group was found:

$$\tau_H = (1.65 \pm 0.4).10^{-12} \text{ s}.$$  

This value is about four times smaller than the correlation time obtained by Meier et al. for proton exchange mechanism in p-toluic acid.

5. D$_0$ compound.

5.1 PLASTIC PHASE. — Spectra recorded with the fully protonated D$_0$ compound reflect all the motions analysed above with the D$_1$ compound or from the difference $D_0-D_{10}$ and should confirm our conclusions of §§3 and 4.

Figure 14 shows a comparison of the spectra obtained with D$_0$ at a momentum transfer $Q = 1.32$ Å$^{-1}$ to the corresponding spectrum measured with D$_1$.
The main difference lies essentially in the amount of purely elastic scattering as predicted by the respective EISF variations. The larger elastic intensity for D_0 occurs from the part of the scattering (10%) related to the motion of the carboxylic group, whose EISF remains important (Fig. 13) even at large Q values. The quasi-elastic broadenings are, however, similar. This confirms that the deuteration of the carboxylic group does not significantly affect the dynamics of the t-butyl part of the molecule.

Experimental EISF values were extracted from the spectra, using the above mentioned method and fitting (3) based upon the model taking into account uniaxial rotational diffusion of t-butyl groups and 180° carboxylic group reorientations. Like in the analysis of the D_1 compound, the inelastic contribution was approximated by a single broad Lorentzian function (Eq. (4)). The results are indicated in figure 15 with final values of the f(Q) factors close to 1 for all values of Q, for the three wavelengths of experiment.

![Fig. 15. EISF variations as function of the momentum transfer, Q, for the fully hydrogenated D_0 compound. 60° jumps for t-butyl and 180° jumps for carboxylic group have been considered. Methyl groups are fixed (LEM conformation). Bragg peak positions are indicated by vertical arrows. Symbols are experimental EISF values f(Q).Ao(Q). Squares circles and triangles correspond to λ = 5.9 Å, 5.1 Å and 4.1 Å, respectively.](image)

Following the D_1-analysis, a second experimental EISF was evaluated, including the inelastic contribution in the quasielastic term, according to (5). These values were compared with the theoretical variations predicted by the model based on uniaxial rotational diffusion of the t-butyl about their own axis together with fluctuations of the dimer unit axis. A mean amplitude Δα ≈ 10° was found for the fluctuation, in agreement with the conclusions of the D_1 analysis.

The inelastic part of the spectra was analysed in the P(α, β) representation in a similar manner as for the D_1 isotope. No difference was encountered. Especially the vibrations attributed to the eight membered rings are not modified. These were revealed with the D_1 compound because they involve displacements of the different parts of the dimer unit with respect to each other, and are slightly affected by the mass change induced by the isotopic substitution of the acid proton. Furthermore, the analysis of the low-frequency part of the spectra in terms of an overdamped oscillator provides values of the frequency ω_0 and of the damping coefficient γ in accordance with those obtained from the D_1 analysis. These values of ω_0 coincide perfectly with the curve illustrated in figure 8. They are not reported to simplify the illustration.

Even when refining simultaneously all spectra recorded at the same temperature with the same incident energy, it is impossible to obtain precise values of the two relevant correlation times related to t-butyl and acid proton, especially if the amount of inelastic scattering is also refined. More precisely, the correlation time for acid proton τ_H, which is related to the smaller quasi-elastic structure factor, has a very small weight in the theoretical function under test. Therefore it tends to become unrealistic, tending to make the theoretical function account of some experimental inaccuracy. Therefore the value obtained with the D_0 and D_10 compounds was introduced as parameter in the refinements and kept fixed τ_H = 1.65 × 10^{-12} s for all the temperatures. Final values for τ_H are reported in figure 17. For the data recorded with the incident wavelength λ = 5.9 Å, at T = 303 K, it was possible to obtain for the methyl motion a correlation time τ_M = (0.95 ± 0.5) × 10^{-10} s, but, like the value obtained from the D_1 analysis, severe reserves have to be made concerning the meaning of this value.

![Fig. 16. Experimental EISF values (points), in the case of the D_0 compound, at T = 330 K, in the liquid state. These are compared with theoretical variations as function of Q predicted by models based on overall tumbling of monomers or dimer units.](image)

5.2 LIQUID PHASE. — An experiment was performed at T = 330 K, for the D_0 compound, in the liquid phase of pivalic acid. Experimental values of the
EISF were extracted. They are reported in figure 16. It is noteworthy that for $Q = 0$, the experimental EISF tends to 1, indicating that, on the instrument time scale no translational diffusion is visible. Furthermore, the liquid phase of pivalic acid is known to be essentially composed of molecules associated in dimer units.

![Fig. 17. — Correlation times for t-butyl motions in pivalic acid, versus reciprocal temperature. Open symbols represent results of refinements with D$_1$ compound, full symbols correspond to D$_0$. Squares, triangles and circles are used for $\lambda = 5.9$ Å, 5.1 Å and 4.1 Å, respectively.](image)

Experimental EISF values lie on the theoretical curve predicted for whole-dimer tumbling (or nearly above). Therefore it seems that, in the liquid phase, strong correlations still exist between pivalic molecules whose mass centre remain fixed (on the IN6 time scale). Molecules undergo overall rotation about the dimer mass centre which remains in a finite small region of space. This is confirmed by the EISF value at $Q = 1.32$ Å$^{-1}$ which lies definitely above the neighbours. Considering the existence in the plastic phase of two Bragg peaks at $Q = 1.23$ Å$^{-1}$ (111) and $Q = 1.44$ Å$^{-1}$ (200), the excess of elastically scattered intensity at $Q = 1.32$ Å$^{-1}$ confirms the existence of a residual long range order in the liquid phase.


In the low-temperature phase, just below the transition ($T = 278$ K) a small quasi-elastic broadening is still visible (about 10% of the instrument resolution). Determination of an experimental EISF by the method already used in §§ 3 and 4 is very imprecise. It was shown in [11] that in this phase, the motions consist of 120$^\circ$ jumps of both methyl and t-butyl groups. Direct refinement of the relevant correlation times $\tau_{M}$ and $\tau_{B}$, is very difficult, but at $T = 278$ K, the global quasi-elastic broadening is in accordance with the value observed by the backscattering technique. When the temperature decreases, this broadening becomes rapidly outside of the instrument energy range, and the Arrhenius laws obtained for $\tau_{M}$ and $\tau_{B}$ cannot be confirmed.

7. Summary and conclusion.

Using the quasi-elastic neutron scattering technique, the dynamics of the different parts of the pivalic acid molecule have been investigated in the plastic phase. The consistency between all the above results obtained using several incident wavelengths and differently deuterated compounds allow us to be confident in our conclusions.

Three types of motions have been revealed by these experiments in the plastic phase: (i) reorientations of the t-butyl groups by 60$^\circ$ jumps about their threefold axis, (ii) reorientations of the eight-numbered carboxylic ring linking two molecules to form a dimer, (iii) fluctuations of the dimer-axis orientation about [110] lattice directions. In addition the existence of reorientations in the low-temperature phase (already observed by the backscattering technique) has been confirmed.

From the analysis of both D$_1$ and D$_0$ compounds, the determination of an experimental EISF is consistent with a model allowing 60$^\circ$ jumps of the t-butyl groups. This result is in accordance with the conclusions of the crystal structure study [2], according to which the molecules can occupy two discernible equilibrium positions about each [110] lattice direction. In fact it was shown that this motion can also be described in terms of a uniaxial diffusion. The activation energy associated to that motion if $\Delta H = 12$ kJ/mol.

Large fluctuations of the orientation of the long axis of whole-dimer units were evidenced. These were first described in terms of a random diffusion of the dimer axis with a sharp angular distribution peaked along [110] directions. The width of this distribution was found equal to about 10$^\circ$. From the analysis of the inelastic part of the spectra, another description was proposed. Motions of the dimer axes were analysed in terms of overdamped librations. The average value of these librations was found equal to about 8$^\circ$, in good agreement with the first description.

From the measurements carried out with both D$_9$ and D$_{10}$ compounds, the dynamical behaviour of the acid proton could be analysed. Experimental EISF values are consistent with 180$^\circ$ jumps of the carboxylic groups about the dimer axis. A description on a basis of a double proton exchange mechanism can be excluded, at least if this motion is considered alone. However, the possibility of simultaneous reorientation and proton-exchange processes cannot be ruled out. We intend to perform further experiments on a more extended $Q$-range and using a better instrument resolution in order to elucidate this point.

Methyl group motions were found too slow to produce quasielastic broadening, except perhaps with
A = 5.9 Å, and they appear to have no change at the phase transition.

A similar behaviour has been found with other t-butyl compounds [25, 26], where rotation of methyl groups about their threefold axes and rotation of the entire t-butyl group take place at similar though not identical rates at low-temperatures. The phase transition is found to be associated with a drastic change in the dynamics of the t-butyl group, whilst the motion of methyls appears unaffected. The intramolecular nature of the potential acting on CH₃ groups was also evidenced in other trimethyl compounds [27, 28]. Conversely, the trimethyl groups experiences an intermolecular potential which largely depends on the crystal structure. In the case of trimethylsulfoxonium iodide, this potential is so strong that cation reorientations are too slow to produce any quasielastic broadening in the backscattering experiment [28].

From the analysis of the inelastic part of the spectra a question arises. Torsional vibrations are observed at 256 and 263 cm⁻¹ for CH₂ groups and 185 cm⁻¹ for CD₃ groups, in accordance with Raman results. Within the harmonic oscillator approximation, we can calculate a potential barrier of about 16 kJ/mol, a value appreciably larger than found from neutron and NMR analyses (9.8 kJ/mol). Neither second moment or T₁ measurements can distinguish between CH₃ or t-butyl rotations and in the interpretation of NMR data the methyl motion was a priori assumed faster than the t-butyl motion. IQNS technique is in principle able to make the distinction. In fact, whilst neutron measurements led to the same conclusions and the same values of the activation energy than NMR, it cannot be excluded that the rather poor statistics of the backscattering data prevents the refinements to converge to the correct parameters-values, especially if starting from an inverted ratio of the jump-rates for methyl and t-butyl.

Previous NMR studies of t-butyl cyanide and several t-butyl halides [25, 26] disagree with the conclusions of neutron analyses [29], recently confirmed from ²H NMR analysis [30], of a slower rate for methyl jumps.

We have reanalysed our previous data, starting from the inverse assumption concerning the ratio of the jump-rates. It is possible, effectively to converge to values of the correlation times corresponding to a much slower dynamics for methyl groups than for t-butyl groups. Moreover, the activation energy deduced from an Arrhenius plot of the CH₃ correlation times as a function of the reciprocal temperature is more in agreement with the potential barrier of 16 kJ/mol suggested from inelastic neutron scattering. Then, conclusions of [11] concerning the jump-rates and especially the Arrhenius plot of figure 6 seem erroneous. However, because of the poor statistics it was impossible, on the single basis of these data, to make the proof of this mistake, except that the slow-methyl hypothesis is more in accordance with the results of the present work.

Therefore, we intend to perform other high-resolution backscattering-measurements in both the low-temperature and plastic phases of pivalic acid, in order to analyse the dynamical behaviour of methyl-groups at the phase transition in conjunction with a ²HNMR analysis.

The tumbling motion is not visible with IN6, in accordance with the value of the correlation time (τ ≈ 10⁻⁹ s) obtained from NMR [5, 6]. It is noteworthy that the isotopic molecular reorientation is much longer in pivalic acid than those in other undimerized plastic crystals. Recently, we performed another IQNS experiment with hexamethylethane (CH₃)₃CC(CH₃)₃ in which two t-butyl groups are linked together. Marked differences were found with respect to the pivalic acid case. Essentially, the whole-molecule tumbling motion is visible before the melting point. In fact, pivalic dimer units are more elongated in shape than the hexamethylethane molecules, and it appears realistic that the steric hindrance against overall reorientations is important. Individual monomer tumbling requires the breaking of two hydrogen bonds, and should occur on a longer time-scale.

Actually, the exact mechanism of the tumbling motion has yet to be elucidated. We have just performed another IQNS measurement with improved instrument resolution, using the backscattering spectrometer, IN10, of the Institut Laue-Langevin. The translational self-diffusion of the molecules is too slow to be taken into the consideration but an EISF analysis should decide unambiguously between the two hypotheses : whole-dimer or individual monomer reorientations. However, great care has to be taken in that determination because most of the scattered intensity (= 90 %) lies outside the instrument range. Therefore, the statistics is poor and furthermore methyl groups motions should occur on a time-scale. We shall report on these results in a forthcoming paper.

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