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I. Incoherent neutron scattering law for dynamically independent molecular and intramolecular reorientations

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Résumé. — Les réorientations de tout ou parties de la molécule d'acide pivalique ont été étudiées dans les deux phases solides (transition de phase à 279.9 K) par diffusion neutronique quasiélastique incohérente. Différents modèles de sauts sont développés en vue de leur comparaison avec les résultats expérimentaux. Des modèles de sauts réorientations simples sur N sites également répartis sur un cercle, peuvent être utilisés pour le mouvement du groupement méthyle ou celui du groupe carboxylique. Si des rotations du t-butyle apparaissent en même temps que des rotations des méthyles, un modèle de saut plus élaboré est développé sur la base de mouvements de réorientations autour de deux axes différents et dynamiquement non couplés. Enfin, nous envisageons le cas où un mouvement de basculement de toute la molécule est adjoint aux deux mouvements précédents et une loi approchée est donnée pour la diffusion correspondante.

Abstract. — Reorientations of the pivalic acid molecule and/or of its parts have been studied in the two solid phases (phase transition at 279.9 K) by incoherent quasielastic neutron scattering (IQNS). Different jump-models are developed for comparison with the experimental results. For methyl-group or carboxylic-group motion, simple reorientational jump models among N sites over a circle can be used. When t-butyl rotations together with internal methyl rotations occur simultaneously, a more sophisticated jump model is developed based upon dynamically uncorrelated reorientational motions about two different axes. Finally we consider the case when a tumbling motion of the whole-molecule is added to the two previous motions and an approximate scattering law is also derived.

1. Introduction.

In the study of condensed molecular phases, « plastic crystals » are of particular interest. These are orientationally disordered crystals, but with translational order. Such crystalline phases are generally characteristic of globular or highly symmetrical molecules, or of molecules containing mobile groups. In the former case, rotational jumps of the whole molecule, among a set of equilibrium orientations, are often observed. This leads to the apparent (statistical) high symmetry of the crystal. As the temperature is increased, the rate of the jumps also increases, large librations occur and the motion becomes more isotropic. In some cases it is possible to give an adequate description of the molecular motion in terms of the rotational diffusion model. Various experimental techniques are used in the investigation of these phases : in particular Incoherent Quasielastic Neutron Scattering (IQNS). Among the examples of rigid, quasi-spherical molecules investigated with this method, let us mention adamantane [1, 2] and its derivatives [3, 4], quinuclidine [5] and bicyclo-octane [6, 7]. In contrast, a number of molecules with fairly low symmetry also form plastic phases. This is the case for non-rigid molecules with internal rotational degrees of freedom, as for instance t-butyl cyanide [8], where methyl groups or whole t-butyl groups rotate. A similar case is encountered with trimethylammonium chloride [9, 10]. More complex cases can also be encountered, as for example succinonitrile [11-14] where an isomerization mechanism between two gauche and a trans conformers and rotation of the trans isomer as a whole occur simultaneously.

Pivalic acid (Fig. 1) (CH₃)₃CCOOH (also called trimethylacetic acid or 2,2-dimethylpropanoic acid) is another particularly interesting example. This compound undergoes a solid-solid phase transition at...
The pivalic acid molecule. Two conformations are shown, referred to as LEM and CALDER, depending on the orientation of methyl groups.

\[ T_m = 279.9 \text{ K} \ (\Delta S_m = 7.1 \text{ cal mol}^{-1} \text{ K}^{-1}) \] between a low-temperature triclinic phase [15] and a high temperature orientationally disordered phase, which subsists up to the melting point \( T_m = 308.5 \text{ K}, \Delta S_m = 1.8 \text{ cal mol}^{-1} \text{ K}^{-1} \). X-ray studies [16, 17] have established that the crystal structure is face-centred-cubic, with the unit cell parameter \( a = 8.87 \pm 0.03 \text{ Å} \), containing four molecules in the unit cell. The molecular symmetry is consistent with the crystal symmetry corresponding to different possible equilibrium positions of a molecule. The central C-C axes of the molecules lie along either of the \( \langle 110 \rangle \) directions of the lattice. Under these conditions, the most probable location of the carboxylic group (assumed to be planar) is in the corresponding (001) plane.

Figure 1 shows the pivalic acid molecule. Depending on the precise position of the hydrogen atoms of the three methyl groups, two configurations are plausible (referred to as LEM [18] or CALDER [19]). Thus assuming two equilibrium positions related by 180° rotations around the \( \langle 110 \rangle \) directions, the space group is Fm3m. The dynamical properties of this phase have been the subject of intensive study by various techniques. Dielectric relaxation measurements [20] have led to the hypothesis of the existence of non-polar dimer units in the plastic phase (two next-neighbouring molecules of pivalic acid linked by two hydrogen-bonds). On passing the melting point, only a small change in the dielectric constant was observed, and it was suggested that the molecular rotational motion is comparable in the plastic phase to that in the liquid.

Measurements of the nuclear magnetic relaxation times provide information about the nature of both translational diffusion and rotational motion of the molecules. R. L. Jackson and J. H. Strange [21] have measured nuclear magnetic spin relaxation times \( T_1, T_2 \) and \( T_{1p} \) for methyl and acid protons in pivalic acid throughout the plastic crystalline phase from 279.9 K to 308.5 K. \( T_{1p} \) and \( T_2 \) of the methyl protons were interpreted in terms of a translational self-diffusion of the molecules, with an activation energy \( E_a = 63 \pm 6 \text{ kJ/mole} \). \( T_1 \) relaxation mechnism was attributed to molecular quasi-isotropic reorientation. The corresponding activation energy was obtained \( E_a = 36 \pm 3 \text{ kJ/mole} \). \( T_{1p} \) and \( T_2 \) measurements for the acid protons show that they are moving through the lattice at a much faster rate than the molecules. This result and the rather high value of the activation energy related to the quasi-isotropic reorientation of the methyl groups suggested that this last motion involves a making and breaking of dimers, thus allowing an exchange of the acid protons to occur between two molecules.

S. Albert et al. [22] performed measurements on the temperature dependence of the spin-lattice relaxation times \( T_1 \) and \( T_{1p} \) in the proton static and rotating frames, respectively, as well as some broad line measurements. They found that in the high-temperature plastic phase (> 280 K), \( T_1 \) is governed by an overall molecular tumbling with an activation energy \( E_a \) of 25.1 ± 0.25 kJ/mole. A self-diffusion of the whole molecule with an activation energy \( E_a \) of 50.2 ± 8.4 kJ/mole is also evident from the spin-lattice relaxation time in the rotating frame \( T_{1p} \).

Assuming that the acid proton can move through the lattice at a much faster rate than the molecular entity, the proton relaxation time should be affected by its motion. On the contrary, the \( T_1 \) of the quaternary carbon is determined mainly via the dipolar interaction with the intramolecular protons. Individual \(^{13}\text{C}\) spin-lattice relaxation time measurements were reported by T. Hasebe et al. [23], in the plastic and the liquid phases. The results were analysed in terms of methyl reorientation, t-butyl reorientation about central C-C axis and isotropic molecular reorientation. It was found that the isotropic reorientation of molecular dimeric units was responsible for the \(^{13}\text{C}\) relaxation in the plastic phase. The corresponding activation energy is \( E_a = 56.4 \pm 6.3 \text{ kJ/mole} \). This value does not agree with the results of the \(^1\text{H}\)-NMR experiments. Such a discrepancy seems to confirm that the migration of the acid protons effectively contributes to the relaxation times of the proton.

The values of the activation energy in the plastic phase for the translational diffusion obtained from \( T_{1p} \) measurements (63 ± 6 kJ/mole [21] and 50.2 ± 8.4 from [22]) do not agree with that found by an earlier radio-active tracer experiment [24]. However, another self-diffusion study have been performed recently [25, 26]. The activation enthalpy obtained in this experiment (59 ± 1 kJ/mole) is in good agreement with values obtained from NMR.

Incoherent neutron scattering permits observation of the proton self-correlation function. Its space-time Fourier transform, the incoherent scattering function, contains all the information about the proton single particle motion, unlike many other techniques. Both dynamical and geometrical information can be obtained. The Elastic Incoherent Structure Factor (EISF) can be determined experimentally as the ratio of the
purely elastic intensity over the sum of elastic and quasi elastic intensity. It gives a direct measurement of the time-averaged spatial distribution of the protons and hence information about the rotational and translational trajectories of the molecules [27]. Then we may conclude what types of motions are sufficiently rapid to be resolved from the (incoherent) elastic peak, and propose a physical model to be compared to the observed quasi-elastic spectra. We have recently performed IONS measurements in the low temperature phase of pivalic acid, and the existence of a dynamical disorder was unambiguously proved. The experimental EISF was interpreted in terms of 120° jumps of both methyl and t-butyl groups about their respective threefold axes. Correlation times were deduced for each motion, which were in fair agreement with NMR results [22]. To obtain more detailed information about the reorientations in pivalic acid, we have performed new IQNS measurements, in both the low and high-temperature phases. As the main contribution to the incoherent scattering occurs from the hydrogen atoms of the molecule \( \sigma_{\text{inc}} \approx 80 \text{ barns} \), different partially deuterated compounds were used in these experiments.

The compound with deuterated carboxylic group \((\text{CH}_3)_3\text{CCOOHD}\) (hereafter referred to as \(\text{D}_1\)) would allow us to study the motions of the t-butyl group, i.e. methyl rotations and t-butyl reorientations about the central C-C axis, or whole-molecule tumbling. In contrast, when deuterating the t-butyl group, \(((\text{CD}_3)_3\text{CCOOH}\) compound, referred to as \(\text{D}_9\), the scattering is essentially due to the H acid proton. This enabled carboxylic group rotation about the central C-C axis, together with whole-molecule tumbling to be investigated. Although the main part of the scattered intensity occurs from the single hydrogen, the contribution of the other atoms (coherent as well as incoherent) is not negligible. « Background » measurements have to be made using the fully deuterated compound \((\text{CD}_3)_3\text{CCOOD}\) (referred to as \(\text{D}_{10}\)). Finally, results obtained from \(\text{D}_9\) and \(\text{D}_1\) have to be consistent with experimental results with the fully protonated molecule \((\text{CH}_3)_3\text{CCOOH}\) (referred as \(\text{D}_0\)).

Our aim in the part I of this article is to derive the rotational incoherent scattering laws corresponding to different combinations of possible motions for methyl, t-butyl, carboxylic groups or whole-molecule allowed in the plastic and in the low temperature phases, for \(\text{D}_0\), \(\text{D}_1\), \(\text{D}_9\) and \(\text{D}_{10}\) compounds. A detailed analysis of the experimental results is given in the part II of this paper.

2. Incoherent quasielastic neutron scattering.

IQNS from hydrogogenous organic molecules provides a powerful way of investigating the motions of one individual proton and thereby, those of the molecule itself. The double differential incoherent cross-section gives the proportion of neutrons with incident wave-vector \(k_0\) scattered by a molecule into an element of solid angle \(d\Omega\) around the direction \(k\) with an energy exchange between \(\hbar\omega\) and \(\hbar(\omega + d\omega)\)

\[
\frac{\partial^2 \sigma(k, k_0)}{\partial \Omega \partial \omega} = \frac{k}{k_0} \sum_{j=1}^{N} \sigma_{\text{inc}} \frac{S_{\text{inc}}'(Q, \omega)}{S_{\text{inc}}(Q, \omega)}
\]

where the sum runs over all the incoherent scatterers of the molecule. \(Q = k - k_0\) is the wave-vector transfer. \(S_{\text{inc}}'(Q, \omega)\) is the incoherent scattering function for atom \(j\). We can define a normalized mean incoherent scattering function \(S_{\text{inc}}(Q, \omega)\) by one atom of the molecule

\[
\frac{\partial^2 \sigma(k, k_0)}{\partial \Omega \partial \omega} = \frac{k}{k_0} \sigma_{\text{inc}} S_{\text{inc}}(Q, \omega)
\]

where

\[
\sigma_{\text{inc}} = \sum_{j} \sigma_{\text{inc}}.
\]

Let us denote by \(S_{\text{inc}}(Q, \omega)\) the normalized mean incoherent scattering function for one hydrogen or deuterium belonging to the t-butyl part of the molecule and by \(S_{\text{Ac}}(Q, \omega)\) that for the acid hydrogen or deuterium of the carboxylic group. \(\sigma_{\text{inc}}(H)\) and \(\sigma_{\text{inc}}(D)\) are the incoherent cross-section for hydrogen and deuterium, respectively. The incoherent cross-sections for both carbon and oxygen can be neglected. Then the mean scattering function, for each of the deuterated compounds, is written

\[
\begin{align*}
D_0 &\quad S_{\text{inc}}^0(Q, \omega) = \frac{9}{10} S_{\text{Ac}}(Q, \omega) + \frac{1}{10} S_{\text{inc}}(Q, \omega) \\
D_1 &\quad S_{\text{inc}}^1(Q, \omega) = \frac{9}{10} \frac{\sigma_{\text{inc}}(H)}{\sigma_{\text{inc}}(D) + 9 \sigma_{\text{inc}}(H)} S_{\text{Ac}}(Q, \omega) + \frac{\sigma_{\text{inc}}(D)}{\sigma_{\text{inc}}(D) + 9 \sigma_{\text{inc}}(H)} S_{\text{inc}}(Q, \omega) \\
D_9 &\quad S_{\text{inc}}^9(Q, \omega) = \frac{9}{10} \frac{\sigma_{\text{inc}}(H)}{\sigma_{\text{inc}}(H) + 9 \sigma_{\text{inc}}(D)} S_{\text{Ac}}(Q, \omega) + \frac{\sigma_{\text{inc}}(H)}{\sigma_{\text{inc}}(H) + 9 \sigma_{\text{inc}}(D)} S_{\text{inc}}(Q, \omega) \\
D_{10} &\quad S_{\text{inc}}^{10}(Q, \omega) = \frac{9}{10} S_{\text{Ac}}(Q, \omega) + \frac{1}{10} S_{\text{inc}}(Q, \omega).
\end{align*}
\]
Equations (3a) and (3d) are formally similar but the experimental values are different as they correspond respectively to completely hydrogenated (D₀) and deuterated (D₁₀) molecules.

Clearly, the second term in the expression of \( S_{\text{inc}}(Q, \omega) \) can be neglected and the scattering from the D₁ compound will essentially reflect the dynamics of the t-butyl group. On the contrary, although the intensity, scattered from the t-butyl part of the D₀ molecule is small, it cannot be neglected. Nevertheless, information about the dynamics of the carboxylic group can be obtained by combining (3c) and (3d). However, the difference technique is not trivial as we shall see in part II of this paper.

The motions in which the protons of a molecule are involved are:

i) molecular vibrations like internal deformations and librational oscillations about their equilibrium positions,

ii) lattice vibrations (collective displacements of the mass centres of the molecule),

iii) reorientational jumps of the whole molecule and/or of its parts.

Clearly, taking into account the experimental resolution, translational self-diffusion of the molecules is too slow to be considered here [21, 22, 25, 26].

Neglecting the existence of any coupling between these three kinds of motions, the incoherent scattering functions, \( S_{\text{inc}}(Q, \omega) \), can be written (for one atom):

\[
S_{\text{inc}}(Q, \omega) = \exp(-2W) \left( S_{\text{inc}}^R(Q, \omega) + S_{\text{inc}}^\nu(Q, \omega) \right).
\]  

(4a)

The term \( \exp(-2W) \) is a Debye-Waller factor which, with \( S_{\text{inc}}^\nu(Q, \omega) \), accommodates both the lattice vibrations and the molecular vibrations. The inelastic term:

\[
S_{\text{inc}}^R(Q, \omega) = \exp(-2W) S_{\text{inc}}^\nu(Q, \omega)
\]  

(4b)

usually contributes only little to the scattered intensity in the quasielastic region. In that case it can be approximated by a one-phonon expansion using a Debye density of state [11, 12]. However in the case of pivalic acid it will be shown in paper II that this term is of particular importance and cannot be neglected. This term will be evaluated in the following.

The rotational incoherent scattering function, \( S_{\text{inc}}^R(Q, \omega) \), contains the effects due to the rotational motions of the molecule.

The time Fourier transform

\[
I_{\text{inc}}(Q, t) = \frac{1}{2\pi} \int S_{\text{inc}}^R(Q, \omega) \exp(i\omega t) d\omega
\]  

(5a)

is the intermediate rotational scattering function, given by [27]

\[
I_{\text{inc}}(Q, t) = \sum_{D_0} \sum_i \exp \left\{ iQ[r(Q) - r(O_0)] \right\} \times P(O_0, Q, t) P(O_0).
\]  

(5b)

The sums are taken over all initial (\( O_0 \)) and final (\( Q \)) equilibrium orientations (and eventually, internal conformations) of the molecule. \( r(Q) \) is the position vector of the scatterer being considered, for the orientation \( Q \). \( P(O_0, Q, t) \) is the conditional probability of finding the molecule at time \( t \), in the orientation \( Q \), if it was in \( O_0 \) at time, \( t = 0 \). \( P(O_0) \) is the distribution of the initial orientations.

Our aim in this part I is to evaluate the quasielastic rotational scattering functions related to different possible combinations of reorientations of the whole molecule and/or of its parts. However before we shall return to these calculations, the following remark is noteworthy.

In IQNS experiments from hydrogeneous compounds, the neutron mean free-path in the sample is often comparable with the macroscopic dimensions of the specimen. The experimental spectra also contain small contributions from neutrons which have been scattered several times. This effect is ignored in the expressions like (6) after, which assumes that, once scattered, the neutron leaves the sample without being adsorbed or further scattered. For more information about multiple-scattering effects, see [28] and references therein.

3. Uniaxial reorientational jump models: rotation of methyl or carboxylic groups only.

Let us first consider the cases where the proton moves about one molecular axis alone, as for instance when internal reorientations of the methyl groups or reorientations of the t-butyl group without inner methyl rotation only occur.

The disorder of the molecule itself between the \( <110> \) lattice directions will be considered as static. This assumption does not rule out the possible existence of a tumbling motion, but simply assumes that it is sufficiently slow to be outside the instrument range.

In the case of a polycrystalline sample, the rotational scattering function for one proton, given by a jump model between \( N \) equilibrium positions equally spaced on a circle of radius \( r \), can be written as [29, 30]:

\[
S_{\text{inc}}^R(Q, \omega) = a_0(Q) \delta(\omega) + \frac{1}{\pi} \sum_{i=1}^{N-1} a_i(Q) \frac{\tau_i}{1 + \omega^2 \tau_i^2}
\]  

(6a)

with

\[
a_i(Q) = \frac{1}{N} \sum_{n=1}^{N} j_0 \left[ 2Kr \sin \left( \frac{\pi n}{N} \right) \cos \left( \frac{2\pi n}{N} \right) \right]
\]  

(6b)

\( j_0(\cdot) \) is the spherical Bessel function of order zero.
The terms:
\[
\frac{1}{\pi} \frac{\tau_i}{1 + \omega^2 \tau_i^2} = L_i(\omega)
\]
are the normalized Lorentzian functions of energy transfer \(\hbar \omega\). Their half-widths at half maximum (hwhm) involve the jump rates \(\tau_i^{-1}\).

As in any case when the molecular motions are localized in space, the incoherent quasielastic rotational function exhibits a purely elastic component \(a_0(Q) \delta(\omega)\). The coefficient \(a_0(Q)\) is the mathematical expression of the Elastic Incoherent Structure Factor (EISF) giving information about the geometry of the rotational motion of the molecule via the time-averaged spatial distribution of the proton. By extension, the coefficients \(a_i(Q)\) appearing in the quasielastic term are called quasielastic structure factors.

The hwhm \(\tau_i^{-1}\) of the Lorentzian functions are defined by:
\[
\frac{1}{\tau_i} = \frac{2}{\tau} \sin^2 \frac{\pi l}{N}.
\]

The residence time, \(\tau\), is the mean-time spent between two successive jumps of the proton. Equation (7) assumes that only \(\pm 2 \frac{\pi}{N}\) rotations occur. Taking into account the possible existence of rotational angles which are multiple of \(2 \frac{\pi}{N}\) requires the use of group theory [31, 32].

It is noteworthy that as a \(2 \frac{\pi}{N}\) rotation and a \(-2 \frac{\pi}{N}\) rotation have an equal probability to occur, some characteristic times evaluated from (7) are equal, and the corresponding structure factors can be added together.

In figures 2 to 4, elastic and quasielastic structure factors for different models of uniaxial reorientations in the pivalic acid molecule are illustrated. Their expressions are reported in table I, together with the relevant characteristic times. In fact, a large variety of physical situations can be imagined, when referring to the conclusions of IQNS studies of other compounds where three methyl groups are bounded to the same atom.

In the case of trimethyloxosulfonium ion, the quasielastic broadening essentially results from methyl group \(120^\circ\)-reorientations. These were found to play no part in the successive phase transitions [33, 34]. The low temperature phase of pivalic acid is triclinic [15] and the dynamical disorder has to be analysed in terms of undistinguishable equilibrium positions [34]. The first hypothesis assumes that only reorientations of methyl groups are visible in the IN6 range, in the plastic phase, with only a small change at the phase transition. In figure 2 the structure factors are illustrated, in both cases of \(120^\circ\) or \(60^\circ\) jumps of the methyl groups (Table I) (models \(M_3\) or \(M_6\)). Conversely, in the case of t-butyl cyanide [35] and t-butyl halides [37], [38] it was concluded that the correlation time for methyl rotation was longer than that for t-butyl rotation, in

Fig. 2. — \(D_1\) compound. Elastic (EISF) and quasielastic structure factors in the cases of uniaxial \(120^\circ\)-jumps or \(60^\circ\)-jumps of the methyl groups (Table I) (models \(M_3\) or \(M_6\)).

Fig. 3. — \(D_1\) compound. Elastic and quasielastic structure factors in the case of \(120^\circ\) or \(60^\circ\) jumps of the t-butyl groups (models \(B_3\) or \(B_6\)). The methyl groups are fixed. The two possible configurations have been considered (full line : LEM ; dashed line : CALDER).

Fig. 4. — \(D_9\) compound. Elastic and quasielastic structure factors in the cases of uniaxial \(180^\circ\)-jumps or \(90^\circ\)-jumps of the acid proton (Table I), or in case of a proton exchange mechanism.

The terms:
\[
\frac{1}{\pi} \frac{\tau_i}{1 + \omega^2 \tau_i^2} = L_i(\omega)
\]
are the normalized Lorentzian functions of energy transfer \(\hbar \omega\). Their half-widths at half maximum (hwhm) involve the jump rates \(\tau_i^{-1}\).

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Table I. — Widths of the Lorentzian functions and expression of the elastic (EISF) and quasielastic structure factors, corresponding to uniaxial rotational jump models between \( N \) sites, for methyl groups and acid proton. The terms \( a_0(Q) \) can be calculated from equations (6). The value \( \tau_0^{-1} = 0 \) corresponding to purely elastic scattering has been added to the others calculated from (7). This would correspond in equation (7) to the case \( l = 0 \) or \( l = N \) i.e., where the proton remains fixed or undergoes a jump returning it to its original position.

<table>
<thead>
<tr>
<th>( \frac{1}{\tau_0} )</th>
<th>( \frac{1}{\tau_1} )</th>
<th>( \frac{1}{\tau_2} )</th>
<th>Methyl group or t-butyl group</th>
<th>N = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{1}{\tau_2} = \frac{1.5}{\tau} )</td>
<td>( \frac{1}{\tau_5} = \frac{0.5}{\tau} )</td>
<td>( A_0(Q) = a_0(Q) = \frac{1}{3} [1 + 2j_0(Qr_M\sqrt{3})] )</td>
<td></td>
</tr>
<tr>
<td>( A_1(Q) = a_1(Q) + a_2(Q) = \frac{2}{3} [1 - j_0(Qr_M\sqrt{3})] )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| \( \frac{1}{\tau_0} = 0 \) | \( \frac{1}{\tau_5} = \frac{0.5}{\tau} \) | \( \frac{1}{\tau_4} = \frac{1.5}{\tau} \) | Methyl group \( N = 6 \) or t-butyl group | N = 6 |
| \( A_1(Q) = a_1(Q) + a_3(Q) = \frac{1}{6} [2 + 2j_0(Qr_M) - 2j_0(Qr_M\sqrt{3}) - 2j_0(2Qr_M)] \) |
| \( A_2(Q) = a_2(Q) + a_4(Q) = \frac{1}{6} [2 - 2j_0(Qr_M) - 2j_0(Qr_M\sqrt{3}) + 2j_0(2Qr_M)] \) |
| \( A_3(Q) = a_3(Q) = \frac{1}{6} [1 - 2j_0(Qr_M) + 2j_0(Qr_M\sqrt{3}) - j_0(2Qr_M)] \) |

| \( \frac{1}{\tau_0} = 0 \) | \( \frac{1}{\tau_1} = \frac{2}{\tau} \) | Acid proton \( N = 2 \) or double-well potential | N = 2 |
| \( A_0(Q) = a_0(Q) = \frac{1}{2} [1 + j_0(2Qr_\alpha)] \) |
| \( A_1(Q) = a_1(Q) = \frac{1}{2} [1 - j_0(2Qr_\alpha)] \) |

| \( \frac{1}{\tau_0} = 0 \) | \( \frac{1}{\tau_3} = \frac{1}{\tau} \) | Acid proton \( N = 4 \) | N = 4 |
| \( A_1(Q) = a_1(Q) + a_3(Q) = \frac{1}{4} [1 - j_0(2Qr_\alpha)] \) |
| \( A_2(Q) = a_2(Q) = \frac{1}{4} [1 - 2j_0(Qr_\alpha\sqrt{2}) + j_0(2Qr_\alpha)] \) |

conflict with previous NMR results. Similar conclusions were drawn in the case of trimethylammonium ion [9, 10]. In figure 3 the structure factors related to a model based on t-butyl reorientations alone are illustrated, assuming that the methyl group reorientations are too slow to be visible on the t-o-f experiment time-scale. Whilst X-ray analysis results prove the existence in the low-temperature phase of LEM-configurations alone, the two cases (LEM and Calder) have been considered.

It is noteworthy that in the case of trimethylammonium ion, the quasielastic broadening in the disordered phase above \( T = 308 \) K was interpreted in terms of a rotational diffusion of the whole cation about its threefold axis. Then this model can also be envisaged; the corresponding diffusion law is [27, 29]

\[
S_{\text{int}}(Q, \omega) = J_0^2(Qr \sin \beta) \delta(\omega) + 2 \sum_{l=1}^{\infty} J_l^2(Qr \sin \beta) \frac{1}{\pi} \frac{l^2 D_r}{l^4 D_r^2 + \omega^2}
\]

\( D_r \) is the rotational diffusion constant (uniaxial).
$J_1$ is a cylindrical Bessel function of the first kind. 
$eta$, denotes the angle between the scattering vector $Q$ and the rotation axis. Unfortunately, in the case of a powder specimen, no analytical expression can be given when averaging (8) over all the values of $\beta$. Nevertheless, it is well-known [27], [29] that (6) and (8) lead to practically the same results, if the number of jumps $N \geq 6$ and $Q \leq \pi$. Considering the values of the gyration radius for a proton of a methyl group ($r_M = 0.989 \, \text{Å}$), and for the acid proton ($r_A = 1.10 \, \text{Å}$), this latter condition is fully satisfied, at least in the $Q$-range of the instrument ($Q \leq 2.6 \, \text{Å}^{-1}$).

The rotational diffusion constant $D_\tau$ can be identified with the jump rate $\tau_1^{-1}$ given by (7)

$$D_\tau \approx \frac{1}{\tau_1} = \frac{2}{\eta} \sin^2 \frac{\pi}{N}. \tag{9}$$

We turn now to the analysis of the dynamics of the carboxylic group. Recently IQNS of terephthalic acid [39] together with NMR measurements of p-toluic acid, benzoic acid and several other carboxylic acids [40-44], supported a double proton exchange mechanism amongst the minima of a double well potential between oxygen atoms of the $\text{O-H-O}$ bonds. Conversely, IR analysis of benzoic acid [45] led to the alternative suggestion of $180^\circ$-rotations of the entire hydrogen-bonded eight-membered ring.

In figure 4, the structure factors corresponding to the various models which can be envisaged are illustrated. Their analytic expressions are given in table I, together with those of the related characteristic times.

4. Simultaneous reorientations of methyl and t-butyl groups.

Let us now turn to the calculation of the scattering function when rotations of the methyl groups and of the whole t-butyl group occur together. We shall use the group-theoretical formalism given by Rigny [31], and Thibaudier and Volino [32]. The main hypothesis is that the two kinds of rotations about fixed (crystallographic) and mobile (molecular) axes are uncorrelated, i.e. in our case that the probability per-unit-time of any reorientation of the methyl groups is independent of the precise orientation of the t-butyl group.

4.1 CALCULATION OF THE CORRELATION TIMES. — According to references [31, 32], the relevant correlation times $\tau_\mu$ are given by:

$$\frac{1}{\tau_\mu} = \sum_{\nu} \frac{1}{\tau_\nu} \left( 1 - \chi_\nu^{\mu} \chi_\mu^{\nu} \right) + \sum_{\eta} \frac{1}{\tau_\eta} \left( 1 - \chi_\eta^{\mu} \chi_\mu^{\eta} \right). \tag{10}$$

Here, $\chi_\nu^{\mu}$ is the character of the product of the t-butyl $B_\nu$ and methyl $M_\mu$ rotations in the irreducible representation, $\Gamma_\nu$, of the group product, which is the direct product

$$\Gamma_\nu = \Gamma_{B_\nu} \otimes \Gamma_{M_\mu} \tag{11}$$

of the two irreducible representations $\Gamma_{B_\nu}$ and $\Gamma_{M_\mu}$ of the t-butyl rotation group $G_B$ and of the methyl rotation group $G_M$, respectively. These characters are the products

$$\chi_\nu^{\mu} = \chi_\nu^{B_\nu} \cdot \chi_\mu^{M_\mu} \tag{12}$$

$E$ is the identity operation for the group of t-butyl exchanges. That of the group of methyl rotations is denoted by e. The sums over $\nu$ and $\eta$ run, respectively, over all the classes of these groups. $\tau_\nu$ and $\tau_\eta$ are the correlation times related to rotations $B_\nu$ and $M_\eta$, respectively, i.e. they are the average times between two consecutive $B_\nu$ or two consecutive $M_\eta$ rotations of the same class $\nu$ or $\eta$.

Using the character set for $C^6$ and $C^3$ cyclic groups, evaluation of the correlation times from (10) is straightforward. However, the resulting expressions involve a large number of parameters, namely the correlation times related to each class of both $G_B$ and $G_M$ groups. As it seems a priori difficult to get them all, a further assumption must be made. We shall restrict the possible reorientations for both methyl and t-butyl to jumps from one equilibrium position to a neighbouring one. The relevant correlation times are given in table III for the most general case assuming combinations of $60^\circ$-jumps for both methyl and t-butyl groups. In this table, $\tau_{B_B}$, $\tau_{M_M}$, etc. denote the average times spent between rotations of the same class.

The complex representations which are conjugated together lead to the same values of the correlation times.

4.2 ELASTIC AND QUASIELASTIC INCOHERENT STRUCTURE FACTORS. — For a powder sample the calculations are performed from the general relation:

$$A_\mu(Q) = \frac{\chi_\mu^{\nu}}{\beta} \sum_{\nu} \sum_{B_\nu} \sum_{M_\mu} \exp(iQ \cdot |r - B_\nu M_\mu r|) \tag{13}$$

Table II. — « Reduced » character tables for the different groups $C^6$, $C^3$ (methyl or t-butyl rotations).

<table>
<thead>
<tr>
<th>Classes</th>
<th>$C^6$</th>
<th>$C^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>C_6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>E_1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>E_2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The complex representations which are conjugated together lead to the same values of the correlation times.

Clearly, the relevant correlation times corresponding to other combinations of methyl and t-butyl reorientations can be obtained by getting appropriate characteristic times $\tau_{B_B}$, $\tau_{M_M}$, etc. to zero.

4.2 ELASTIC AND QUASIELASTIC INCOHERENT STRUCTURE FACTORS. — For a powder sample the calculations are performed from the general relation:

$$A_\mu(Q) = \frac{\chi_\mu^{\nu}}{\beta} \sum_{\nu} \sum_{B_\nu} \sum_{M_\mu} \exp(iQ \cdot |r - B_\nu M_\mu r|) \tag{13}$$

(13)
Table III. — Correlation times in the case of a combination of 60°, 120° or 180° for both methyl and t-butyl groups (model B₆ ⊗ M₆). τᵥₜ and τₓₜ are the residence times between two rotations Bᵥ (or Mₓ) of the classes ν (or η).

\[
\begin{align*}
A \otimes A & \quad \frac{1}{\tau_0} = 0 \\
A \otimes B & \quad \frac{1}{\tau_1} = \frac{2}{\tau_{M_6}} + \frac{2}{\tau_{M_2}} \\
A \otimes E_{11}, A \otimes E_{12} & \quad \frac{1}{\tau_2} = \frac{1}{2\tau_{M_6}} + \frac{3}{2\tau_{M_3}} + \frac{2}{\tau_{M_2}} \\
A \otimes E_{21}, A \otimes E_{22} & \quad \frac{1}{\tau_3} = \frac{3}{2\tau_{M_6}} + \frac{3}{2\tau_{M_3}} \\
B \otimes A & \quad \frac{1}{\tau_4} = \frac{2}{\tau_{B_6}} + \frac{2}{\tau_{B_2}} \\
B \otimes B & \quad \frac{1}{\tau_5} = \frac{2}{\tau_{B_6}} + \frac{2}{\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{2}{\tau_{M_2}} \\
B \otimes E_{11}, B \otimes E_{12} & \quad \frac{1}{\tau_6} = \frac{2}{\tau_{B_6}} + \frac{1}{\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{2}{\tau_{M_2}} + \frac{3}{\tau_{M_3}} + \frac{2}{\tau_{M_2}} \\
B \otimes E_{21}, B \otimes E_{22} & \quad \frac{1}{\tau_7} = \frac{2}{\tau_{B_6}} + \frac{3}{\tau_{B_3}} + \frac{3}{\tau_{B_2}} + \frac{2}{\tau_{M_3}} \\
E_{11} \otimes A, E_{12} \otimes A & \quad \frac{1}{\tau_8} = \frac{1}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{2}{\tau_{M_2}} + \frac{2}{\tau_{M_3}} + \frac{2}{\tau_{M_2}} \\
E_{11} \otimes B, E_{12} \otimes B & \quad \frac{1}{\tau_9} = \frac{1}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{2}{\tau_{M_2}} + \frac{2}{\tau_{M_3}} + \frac{2}{\tau_{M_2}} \\
E_{11} \otimes E_{11}, E_{11} \otimes E_{12} & \quad \frac{1}{\tau_{10}} = \frac{1}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{2}{\tau_{M_2}} + \frac{3}{\tau_{M_3}} + \frac{2}{\tau_{M_2}} \\
E_{12} \otimes E_{11}, E_{12} \otimes E_{12} & \quad \frac{1}{\tau_{11}} = \frac{1}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{2}{\tau_{B_2}} + \frac{3}{\tau_{M_3}} + \frac{3}{\tau_{M_3}} + \frac{3}{\tau_{M_3}} \\
E_{21} \otimes A, E_{22} \otimes A & \quad \frac{1}{\tau_{12}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{M_3}} + \frac{3}{\tau_{M_3}} + \frac{3}{\tau_{M_3}} + \frac{3}{\tau_{M_3}} \\
E_{21} \otimes B, E_{22} \otimes B & \quad \frac{1}{\tau_{13}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} \\
E_{21} \otimes E_{11}, E_{21} \otimes E_{12} & \quad \frac{1}{\tau_{14}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{B_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} \\
E_{22} \otimes E_{11}, E_{22} \otimes E_{12} & \quad \frac{1}{\tau_{15}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{B_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} \\
E_{21} \otimes E_{21}, E_{21} \otimes E_{22} & \quad \frac{1}{\tau_{16}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{B_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} \\
E_{22} \otimes E_{21}, E_{22} \otimes E_{22} & \quad \frac{1}{\tau_{17}} = \frac{3}{2\tau_{B_6}} + \frac{3}{2\tau_{B_3}} + \frac{3}{\tau_{B_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} + \frac{3}{\tau_{M_2}} \\
\end{align*}
\]

The sums over ν and η run over all the classes of the t-butyl rotation group and of the methyl rotation group respectively. The two others correspond to summations over all the rotations Bᵥ of the class ν and over all the rotations Mₓ of the class η. g is the order of the group product G₉ ⊗ Gₓ.

This expression has to be calculated for each type of hydrogen in the molecule. Moreover, an average has to be taken over all the possible initial coordinates r. In our case, when considering 120°-jumps for both methyl and t-butyl motions, this leads to two different expressions of the structure factors depending on the molecular configuration LEM or CALDER (see Fig. 1). Such calculations are often performed numerically with the aid of a computer. However, it is possible to obtain analytical expressions. Some remarks can be made:

Given one hydrogen, methyl rotations belonging to the same class (i.e., M₆ and M₆) provide the same set of jump distances, for each t-butyl class, and lead to the same value of the term.

\[
\sum_{B'} j_0(Q | r - B, M_r r |).
\]

Now, two complex representations related to methyl which are conjugated together lead, for each t-butyl class, to two identical structure factors. Moreover, we have seen that their correla-
tion times were equal. Thus, if we take care to multiply the resulting structure factor by 2, only one of them has to be considered.

Taking into account the remarks above, the character tables can be considered only in the « reduced » form given in table II. Explicit expressions of the elastic and quasielastic structure factors are given in table IV for the model based upon 600 jumps for t-butyl and methyl group. Their variation as function of $Q$ is shown in figure 5. The relevant values of the jump distances are listed in table V.

Clearly, putting $\frac{1}{\tau_{B}} = 0$ for every t-butyl rotation and grouping together the structure factors related to identical correlation times, the expressions given in the case of uniaxial rotations of methyl groups alone are found. In the same manner, when setting $\frac{1}{\tau_{Me}} = 0$, expressions corresponding to t-butyl reorientations alone can be obtained easily.

5. Whole-molecule reorientations.
Calculation of the scattering function when whole-molecule tumbling and intramolecular reorientations occur simultaneously would, in principle, require the extension of the method using group theory [31, 32] to the case of three, dynamically uncorrelated jump

Table IV. — Structure factors for the $B_6\otimes M_6$ Model. The notation $J_i$ is a short-hand notation for $j_0(Qr_i)$, where the jump distances $r_i$ are listed in table V.

$$A = \begin{bmatrix} A_0 \\ A_1 \\ \vdots \\ A_{15} \end{bmatrix} = \frac{1}{108} \begin{bmatrix} M & R & P & T \\ M & -R & P & -T \\ N & S & Q & U \\ N & -S & Q & -U \end{bmatrix} \begin{bmatrix} J_1 \\ J_3 \\ J_2 \\ J_4 \end{bmatrix}$$

with

$$M = \begin{bmatrix} 3 & 6 & 2 & 2 & 4 & 1 \\ 3 & 6 & 2 & 2 & 4 & 1 \\ 6 & -6 & 1 & -2 & 2 & -1 \\ 6 & -6 & 1 & -2 & 2 & -1 \end{bmatrix}, \quad R = \frac{1}{2} \begin{bmatrix} 1 & 4 & 2 & 4 & 2 & 2 & 4 & 2 \\ 2 & -4 & 4 & -4 & 4 & -2 & 8 & -2 \\ 2 & -4 & 4 & -4 & 4 & -2 & 8 & -2 \end{bmatrix}$$


$$Q = \begin{bmatrix} 6 & 12 & -4 & -4 & -2 \\ -6 & -12 & 4 & 4 & 2 \\ 12 & 12 & 2 & -4 & -2 \\ 12 & -12 & -2 & 4 & 2 \end{bmatrix}, \quad T = \begin{bmatrix} 1 & 2 & 2 & 2 & 2 \\ -1 & -2 & -2 & -2 & -2 \\ -2 & 2 & -4 & 4 & -4 \\ 2 & -2 & 4 & -4 & 4 \end{bmatrix}, \quad U = \begin{bmatrix} -2 & -4 & 2 & 2 & -4 \\ 2 & 4 & -2 & -2 & 4 \\ 4 & -4 & -4 & 2 & 8 \\ -4 & 4 & 4 & -2 & -8 \end{bmatrix}$$
Table IV (continued).

$$J_1 = \begin{bmatrix} 1 \\ J_2 \\ J_3 + J_{38} \\ J_4 + J_{39} \\ J_5 + J_{40} \\ J_6 + J_{41} \end{bmatrix} \quad \quad J_2 = \begin{bmatrix} J_{17} \\ J_{18} \\ J_{19} + J_{20} + J_{27} \\ J_{21} \\ J_{28} \end{bmatrix}$$

$$J_3 = \begin{bmatrix} J_7 + J_{42} \\ J_8 + J_{43} \\ J_9 + J_{44} \\ J_{10} + J_{11} + J_{45} + J_{46} \\ J_{12} + J_{47} \\ J_{13} + J_{48} \\ J_{14} + J_{49} \\ J_{15} + J_{16} + J_{50} + J_{51} \end{bmatrix} \quad \quad J_4 = \begin{bmatrix} J_{22} \\ J_{23} + J_{29} + J_{31} \\ J_{24} + J_{33} + J_{36} \\ J_{25} + J_{26} + J_{32} + J_{34} + J_{35} + J_{37} \\ J_{30} \end{bmatrix}$$

We shall not consider this general case. In fact, anticipating upon the results of part II, we assume that the t-butyl groups are rigid in the sense that no methyl reorientations are visible on the instrument time scale. Then we are concerned only with reorientations of the t-butyl groups about their threefold axis together with whole-molecule tumbling and the expression (10) can be applied.

In spite of steric hindrance and of the low probability for a reorientation of a dimer as a whole, these calculations were performed for the two different cases of whole-dimer and individual monomer reorientations, the molecules being in their LEM-conformation.

The group for reorientations among lattice directions is O. Since molecules are located along <110> twofold axes, t-butyl reorientations can be restricted to 120° jumps in the EISF calculation (the second set of positions being accessed in the 180° rotation of the O group). In the same manner the rotation group for carboxylic groups was assumed to be C₂. Variations of the EISF of the incoherent scattering law corresponding to a D₀ molecule are shown in figure 6 as function of Q. The EISF corresponding to whole-dimer reorientation has been calculated by assuming that this dimer rotates around one of the two lattice sites corresponding to each of its two monomers. Due to much larger jump distances which are involved, the EISF related to whole dimer reorientations decreases more rapidly than for individual monomer reorientations. Thus neutron scattering should provide a sensitive method to test the hypothesis of breaking and making of hydrogen bonds in the reorientations among the lattice directions.

Really, referring to the NMR results [21, 22], the occurrence of whole-molecule reorientations, on the 10⁻¹¹-10⁻¹² time scale is rather improbable. Conversely, two remarks are noteworthy to consider another...
Table V. — Jump distances for the protons of the t-butyl part of the molecule, when allowing $60^\circ$, $120^\circ$ or $180^\circ$ jumps for both methyl or t-butyl groups (in Å).

<table>
<thead>
<tr>
<th>$r_1$</th>
<th>$r_{11}$</th>
<th>$r_{21}$</th>
<th>$r_{31}$</th>
<th>$r_{41}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.789</td>
<td>3.158</td>
<td>4.030</td>
<td>1.910</td>
</tr>
<tr>
<td>1.714</td>
<td>4.220</td>
<td>3.989</td>
<td>1.068</td>
<td>4.186</td>
</tr>
<tr>
<td>2.482</td>
<td>4.385</td>
<td>4.137</td>
<td>1.014</td>
<td>4.039</td>
</tr>
<tr>
<td>3.016</td>
<td>2.110</td>
<td>2.630</td>
<td>2.075</td>
<td>2.093</td>
</tr>
<tr>
<td>3.654</td>
<td>3.412</td>
<td>1.381</td>
<td>2.323</td>
<td>3.064</td>
</tr>
<tr>
<td>4.196</td>
<td>0.443</td>
<td>2.850</td>
<td>3.391</td>
<td>1.782</td>
</tr>
<tr>
<td>2.866</td>
<td>1.979</td>
<td>2.392</td>
<td>2.299</td>
<td>3.627</td>
</tr>
<tr>
<td>3.740</td>
<td>0.989</td>
<td>3.455</td>
<td>3.625</td>
<td>3.196</td>
</tr>
<tr>
<td>1.433</td>
<td>3.594</td>
<td>3.184</td>
<td>4.010</td>
<td>1.813</td>
</tr>
<tr>
<td>1.890</td>
<td>4.024</td>
<td>3.647</td>
<td>3.141</td>
<td>0.113</td>
</tr>
<tr>
<td>$r_{10}$</td>
<td>3.083</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Oscillations of the dimer axis.

The motion is pictured as follows: the t-butyl groups are assumed to be rigid in such a sense that no methyl reorientation is visible on the time-scale of the instrument. Conversely they are assumed to rotate about their threefold axis, which are coincident with the dimer long axis.

Furthermore, these axes are assumed to oscillate about a common origin, $O$, located on the middle of the central carboxylic ring, as a consequence of deformations of this ring. It is noteworthy that, because we are concerned with incoherent scattering and then we are looking at each proton individually, we could suppose that whole dimers are rigid, rotating about their long axis and simultaneously oscillating about their centre of mass.

The rotation of the hydrogen atoms about the t-butyl axis is considered as uniform. Conversely, these axes fluctuate about the average direction [110] according to the angular, normalized distribution [46]

$$f(\lambda) = \frac{\delta}{2 \sin \delta} \exp(\delta \cos \lambda)$$  \hspace{1cm} (14)

where $\lambda$ is the polar angle of the t-butyl axis with respect to the [110] lattice direction. $\delta$ is a parameter controlling the width of the distribution.

The EISF of this model is easily obtained. In the case of a powder sample, we get, for one proton [46, 47]

$$A_0(\mathcal{Q}) = \sum_{l=0}^{\infty} (2l + 1) j_l^2(QR) S_l^2(\delta) P_l^2(\cos \mu).$$  \hspace{1cm} (15)

Here $j_l(x)$ are the usual Bessel functions. $R$ is the distance of the proton, $M$, to the origin $O$ and $\mu$ is the angle between OM and the t-butyl threefold axis. $P_l(x)$ is the Legendre polynomial of order $l$. 

---

(i) The dimer unit is very elongated in shape. Its momenta of inertia with respect to its principle axes are very different ($I_x = 2117.85$ uma, $I_y = 2036.91$ uma, $I_z = 295.22$ uma). Therefore it can be taken as realistic that rotations about $x$ or $y$ axes are much more hindered than about the $z$-axis. However, due to the large dimension along $z$, small oscillations about $x$ and $y$ are credible and can produce noticeable displacements of the protons of the t-butyl groups, susceptible to be visible in the instrument $Q$ range.

(ii) The eight membered carboxylic ring is not perfectly rigid. As a consequence of the ring deformations, t-butyl groups can perform oscillations with respect to each other.

Consequently, it is worthwhile to introduce a model which takes into account fluctuations of molecules about a particular axis [46, 47].

---

Fig. 6. — $D_0$ compound. Variation of the elastic incoherent structure factor, as function of $Q$, for a model taking into account $120^\circ$ t-butyl, $60^\circ$ methyl ($B_3 \times M_6$) and $180^\circ$ carboxylic group rotations together with reorientations among the <110> lattice directions: the full curve corresponds to whole-dimer reorientations ($T_D$) and the dashed curve to individual monomer reorientations after breaking of the hydrogen bonds ($T_M$).
The $S_i(\delta)$ can be defined as successive order parameters

$$ S_i(\delta) = \left< P_i(\cos \lambda) \right> =$$

$$ = \frac{\delta}{2 \sinh \delta} \int_0^\infty P_i(\cos \lambda) \exp(\delta \cos \lambda) \sin \lambda \, d\lambda. \quad (16)$$

They verify the recurrence relation

$$ S_{i+1}(\delta) = -\frac{2I + 1}{\delta} S_i(\delta) + S_{i-1}(\delta) \quad (17a)$$

with

$$ S_0 = 1 \quad (17b)$$

$$ S_1 = \coth \delta - \frac{1}{\delta}. \quad (17c)$$

The average amplitude of the oscillations can be characterized by the parameter $\Delta \alpha = \cos^{-1}(S_i)$. Furthermore, the case $\delta \to \infty$ (i.e. $S_i(\delta) = 1$) corresponds to a uniform uniaxial rotation of the scatterer over a circle. Conversely, for $\delta = 0$ (i.e. $S_i(\delta) = \delta_{i,0}$) the EISF for a diffusion on a sphere is recovered. Finally, the case $\mu = 0$ corresponds to a scatterer moving over a sphere of radius $R$, on which the distribution is peaked at one point. In that case the EISF is given by

$$ A_0(Q) = \sum_{l=0}^\infty (2l + 1) j_l^2(QR) S_l(\delta). \quad (18)$$

In figures 7 and 8, the EISF evaluated by (16) or (18), are reported, respectively, after averaging over the protons of the dimer unit.

Fig. 7. — EISF variations as a function of the momentum transfer $Q$, for several values of the mean amplitude $\Delta \alpha$ in the case of a model allowing a rotation about the molecular axis and fluctuations of this axis about a mean equilibrium orientation.

Fig. 8. — EISF variations as a function of the momentum transfer $Q$, for different values of the mean amplitude $\Delta \alpha$ in the case of a model allowing only fluctuations of the molecular axis about a mean equilibrium orientation.

7. Inelastic scattering.

We shall restrict to the case of a single scatterer. The inelastic scattering function is written

$$ S_i^{\text{inc}}(Q, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \, dt \times$$

$$ \left\{ \left< e^{iQ \cdot u(t)} e^{-iQ \cdot u(0)} \right> - 1 \right\} \quad (19)$$

where $u(t)$ is the displacement of the scatterer from equilibrium. Referring to usual text books,[48, 49] this term is usually written

$$ S_i^{\text{inc}}(Q, \omega) = Q^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \, dt \times$$

$$ \left< u(t) \cdot u(0) \right> \exp(-2\omega) \quad (20)$$

$S_i(Q, \omega)$ can be evaluated by calculating the dynamical susceptibility. Denoting by $k_B$ the Boltzmann constant and by $T$ the temperature ($\beta = (k_B T)^{-1}$),

$$ S_i^{\text{inc}}(Q, \omega) = \frac{1}{\pi} \chi_{uu}(Q, \omega) \cdot \frac{1}{\exp(\beta \hbar \omega) - 1} \quad (21)$$

where $\chi_{uu}$ denotes the imaginary part (dissipative) of the dynamic susceptibility. This can be defined as the Laplace transform of the response function $K(t)$ [50-52]

$$ \chi_{uu}(s) = \int_0^\infty dt \, K_{uu}(t) \exp(-st) \quad (22)$$

$$ K_{uu}(t) = i \left< [u(t), u(0)] \right> \quad (23a)$$

$$ = iR^2 \left< [\theta(t), \theta(0)] \right> \quad (23b)$$

where $\theta(t)$ is the angular displacement and $R$ the distance of the scatterer to the origin around which
the oscillation occurs. The symbol $[,]$ denotes the commutator. Indeed, for two given quantal quantities, $\theta(t)$ and $\theta(0)$, the time correlation functions $\langle \theta(t) \theta(0) \rangle$ and $\langle \theta(0) \theta(t) \rangle$ are not generally equal.

We have [50]

$$\langle \theta(t) \theta(0) \rangle = \langle \theta(0) \theta(t + i\hbar) \rangle. \quad (24)$$

The time-dependent behaviour of the angle $\theta(t)$ of the dimer unit axis from the mean orientation along [110] lattice direction is assumed to obey the generalized Langevin equation [54, 55]:

$$\ddot{\theta}(t) + \int_0^t \mathcal{M}(t - t') \dot{\theta}(t') dt' + \omega_0^2 \theta(t) = \mathcal{C}(t) \quad (25)$$

where $\mathcal{M}(t)$ is a memory function for $\theta(t)$ and $\mathcal{C}(t)$ a random torque

$$\langle \mathcal{C}(t) \theta(0) \rangle = 0 \quad (26a)$$

$$\langle \mathcal{C}(t) \mathcal{C}(0) \rangle = \mathcal{M}(t). \quad (26b)$$

Now, if we assume that the stochastic torque $\mathcal{C}(t)$ has a significant short correlation time, its correlation function is given by

$$\mathcal{M}(t) = \langle \mathcal{C}(t) \mathcal{C}(0) \rangle = 2 \gamma \delta(t). \quad (27)$$

Hence the Laplace transform

$$m(s) = \int_0^\infty \mathcal{M}(t) \exp(-st) dt = \gamma \quad (28)$$

is equal to the frictional damping.

A derivation of the solution of (26) is given by Lovesey [56]. Introducing the mean square displacement

$$\langle u^2 \rangle = \frac{1}{M} \langle \dot{\theta}^2(0) \rangle \quad (29)$$

where $I$ is the momentum of inertia and $M$ the mass of the scatterer, we get

$$S_{\text{inc}}(Q, \omega) = e^{-2\pi Q^2} \langle u^2 \rangle \cdot \frac{1}{\exp(i\hbar\omega) - 1} \cdot \frac{1}{\pi} \cdot \frac{\omega \gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2}. \quad (30)$$

In figure 9, we have plotted the inelastic scattering law given by (30), as a function of the energy transfer $\hbar\omega_0$ for several values of the damping coefficient $\gamma$.

For small damping the function shows well defined off-centre resonances, corresponding to an oscillatory motion. In other words the dynamic behaviour of the molecule in its potential minimum has essentially a librational character. The position of the peak gives the frequency of the libration and the width is connected with the damping. When the damping increases, the shape of the scattering function gradually changes from a two-peak structure towards a single central peak. Therefore the motion becomes overdamped and essentially diffusive. In that situation, the maximum of the «inelastic» intensity is now located in the neighbourhood of $\hbar\omega = 0$, and the separation of the scattered intensities arising from reorientational and vibrational motions is no more fulfilled.

8. Conclusion.

Different incoherent quasielastic scattering laws have been developed, based upon various jump models for molecular and intramolecular group reorientations. These models will be applied to the data analysis of experimental measurements in the second part of this paper.
References