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NEUTRON SCATTERING STUDY OF METHYL GROUP ROTATION IN SOLID PARA-AZOXYANISOLE (PAA)

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Résumé. — On montre, par diffusion incohérente de neutrons, que dans le PAA solide les groupes méthyle sont animés d’un mouvement de rotation aléatoire autour de leur axe ternaire, et que des rotations, sur la même échelle de temps, autour d’autres axes moléculaires peuvent être exclues. On interprète les spectres quasi-élastiques par un modèle rotationnel figurant des sauts entre trois points équidistants situés sur un cercle de rayon \(a = 1.032 \text{ Å}\). On trouve que le temps moyen entre deux sauts consécutifs varie de \(2.93 \times 10^{-11} \text{ à } 0.95 \times 10^{-11} \text{ s}\) entre 17 et 117 °C, ce qui conduit à une énergie d'activation de \(E_a = 2.54 \pm 0.13 \text{ kcal/mole}\). Le pic intense observé dans le spectre inélastique autour de 31 meV est assigné à la transition \(\nu = 1 \rightarrow \nu = 0\) d’un groupe méthyle se mouvant dans un potentiel sinusoidal à trois puits. On obtient ainsi une barrière \(V_3 = 4.21 \pm 0.37 \text{ kcal/mole}\). Les deux résultats mènent à la conclusion que la forme du potentiel s’écarte notablement de la sinusoidale. On compare ensuite ces conclusions à d’autres résultats expérimentaux. On en déduit, en particulier, que la barrière agissant sur les groupes méthyle provient presque exclusivement de forces intramoléculaires.

Abstract. — Using incoherent neutron scattering, we show that the methyl groups in solid PAA undergo random rotational motion around their three-fold axis, and that rotations about other axes on the same time scale can be excluded. A model for uniaxial rotational jumps between three equidistant sites on a circle of radius \(a = 1.032 \text{ Å}\) is fitted to the quasielastic spectra. The mean jump time \(\tau\) between two consecutive jumps is determined and found to vary from \(2.93 \times 10^{-11} \text{ to } 0.95 \times 10^{-11} \text{ s}\) between 17 and 117 °C, yielding an activation energy of \(E_a = 2.54 \pm 0.13 \text{ kcal/mole}\). The intense peak observed in the inelastic region at 31 meV energy transfer is assigned to the \(\nu = 1 \rightarrow \nu = 0\) torsional frequency of the methyl group in a three-fold potential. For a cosine potential one obtains a barrier \(V_3 = 4.21 \pm 0.37 \text{ kcal/mole}\). Attempts to relate \(E_a\) and \(V_3\) values lead to the conclusion that the potential shape differs appreciably from the cosine form. Our results are then compared with other experimental data. In particular, it seems that the barrier to rotation of the methyl groups arises mainly from intramolecular interactions.

1. Introduction. — Liquid crystalline systems usually present a number of different mesophases which differ by the degree of randomness of the molecular motion. Para-azoxyanizole (PAA) is one of the simpler systems and is perhaps the liquid crystal most extensively studied with the neutron technique during the past few years [1-4]. The difficulty of the interpretation of such neutron data is due to the fact that many different kinds of molecular motion are observed simultaneously and thus are superimposed on one another in the experimental data. In particular this may include effects from the translational diffusion of the molecules, and random rotational motion of whole molecules and/or parts of them. In a series of papers [5-7] we have recently shown how high resolution neutron quasi-elastic scattering (NQES) techniques are favourably combined with partial deuteration of the sample in order to separate different kinds of motion and thereby achieve an unambiguous interpretation of the experimental results. Another important point is that internal molecular random motions may already be observed in the solid phase [6]; such results may then be extrapolated to higher temperature phases and allow the interpretation of
the more complex dynamical phenomena in these phases.

In the present paper we report on NQES experiments performed with two different partially deuterated derivatives of PAA in the solid phase, at a number of different temperatures.

The chemical formulae of the two compounds, which we call PAA-OD4 and PAA-CD3, are:

PAA-OD4

\[
\text{CH}_3 \hspace{1cm} \text{O} \hspace{1cm} \text{N} \hspace{1cm} \text{D} \hspace{1cm} \text{D} \hspace{1cm} \text{O} \hspace{1cm} \text{D} \hspace{1cm} \text{D} \hspace{1cm} \text{D} \hspace{1cm} \text{D}
\]

PAA-CD3

\[
\text{CD}_3 \hspace{1cm} \text{H} \hspace{1cm} \text{H} \hspace{1cm} \text{H} \hspace{1cm} \text{N} \hspace{1cm} \text{N} \hspace{1cm} \text{N} \hspace{1cm} \text{O} \hspace{1cm} \text{D} \hspace{1cm} \text{D} \hspace{1cm} \text{D}
\]

It is seen that spectra of PAA-OD4 will (due to the dominant incoherent scattering cross-section of the proton) mainly contain information on the motion of the two methyl groups. A comparison with the results obtained from PAA-CD3 should permit a separation of the methyl groups' motion from the motion of the whole molecule. We first present the experimental results and interpret the observed quasielastic spectra in terms of random rotational motion of the methyl groups. We then determine the activation energy of this process and try to relate it to the barrier to internal rotation as obtained from inelastic scattering, which is largely due to the torsional oscillation of the methyl groups. Finally, these results are compared to data obtained with other experimental techniques [8], and conclusions are drawn on the nature of the barrier to rotation.

2. Experimental results. — The experiments were performed on powdered samples using the multichopper time-of-flight spectrometer IN5 at the cold source of the ILL-HFR. The isotropy of the material was checked by taking diffraction patterns at two different sample orientations and was found to be satisfactory. In order to obtain information for choosing models of the motions, inelastic data were first taken at 100 °C using an incident wavelength of 8.25 Å (elastic resolution : 48 μeV FWHM) at 9 different scattering angles simultaneously. These angles covered a range of (elastic) momentum transfer of 0.76 ≤ Q ≤ 1.35 Å⁻¹. Care was taken to exclude Bragg scattering. For this reason one of the spectra had to be discarded leaving 8 spectra for comparison with model calculations. The time-of-flight spectra measured under these conditions of PAA-OD4 and PAA-CD3 exhibit striking differences. In figure 1 we show as an example the data for Q = 1.35 Å⁻¹. It is clearly seen that the PAA-OD4 spectrum contains quasielastic scattering underneath a well resolved elastic peak and in addition a prominent inelastic spectrum which is peaked around hω = 31 meV. Upon deuteration of the methyl groups two of these features disappear completely : the quasielastic scattering and the large inelastic peak, leaving only a sharp elastic line and a broad inelastic distribution with relatively low intensity. These observations suggest immediately that the methyl groups are not only involved in a random rotational motion (elastic plus quasielastic scattering) but that in addition they show excitations leading to intense inelastic scattering. In a second series of measurements we have studied the temperature dependence of the observed quasielastic and inelastic spectra of PAA-OD4. We took data for 3 scattering angles simultaneously at 11 different temperatures in the solid phase : 17 ≤ T ≤ 117 °C. In order to improve the resolution a slightly longer wavelength was used (λ₀ = 9.45 Å ; elastic resolution : 32 μeV FWHM). A detailed interpretation of these experimental results will be given below.

3. Models of the motion. — The structure of the PAA molecule suggests that the methyl groups may be involved in one of the following three types of rotational motion:

A) The methoxy group is rotating about the φ-0 bond, the methyl group is not rotating about its C₃ axis.

B) The methoxy group is not rotating, but the methyl group is rotating about its C₃ axis.

C) The methoxy group is rotating about the φ-0 bond and simultaneously the methyl group is rotating about its C₃ axis.
Whereas other authors [9] recently proposed a rotation of the O—CH₃ group (model A or C) with a correlation time of $4 \times 10^{-12}$ s at 60 °C, we will show in the following that on the time scale of the applied neutron technique ($\sim 10^{-10}$ to $10^{-13}$ s), only a model of type B can explain our data.

Since in our experiments on PAA-0D4, the purely elastic peak is well resolved from the quasielastic line, it is convenient to analyze the data in terms of the incoherent elastic structure factor (IESF), $A_o(Q)$, as was done in previous work [5-7]. Let $I_e(Q)$ and $I_q(Q)$ be the elastic and quasielastic intensities, respectively (these two contributions are separated by natural extrapolation and measured by graphical integration), and let $R(Q)$ be the quantity

$$R(Q) = \frac{I_e(Q)}{I_e(Q) + I_q(Q)}.$$

If the scattered intensity comes only from the rotating protons, then $R(Q)$ is an experimental determination of $A_o(Q)$.

The scattering law for a uniaxial rotational model of a proton performing instantaneous jumps between $N$ equidistant sites on a circle of radius $a$ is given in reference [5]. In the case of model B, taking $N = 3$ the scattering law $S_B(Q, \omega)$, for a powder sample, reads:

$$S_B(Q, \omega) = A_o(Q) \delta(\omega) + \frac{1}{\pi} \left[ 1 - A_o(Q) \right] \frac{2 \tau/3}{1 + \omega^2 (2 \tau/3)^2}$$

(2a)

with

$$A_o(Q) = \frac{1}{4} \left[ 1 + 2 j_0(Qa \sqrt{3}) \right].$$

(2b)

In these expressions, $\tau$ is the mean time between two consecutive jumps and $j_0$ is the zero order spherical Bessel function. For model A, the same general theory may be used, but one must average over the three protons which in this case have different gyration radii. Finally model C involves a complex rotational motion of the methyl protons. The $C_3$ axis of the methyl group is inclined by an angle of 62° [10] with respect to the $\varphi$-0 bond (which is very near the molecular axis). The formulae for this case may be taken from reference [11]. We have plotted $A_o(Q)$ for models B and C in figure 2 together with the experimental values of $R(Q)$. It is seen that there is a large difference between the curve for model C and the experiment (model A gives a curve just slightly above that for model C) so that models A and C may be immediately discarded. The curve for model B (methyl rotation only) is slightly but systematically lower than the experimental points. We explain this deviation by additional incoherent elastic scattering due to the nuclei of the phenyl rings (deuterons and a small number of protons because of the non perfect partial deuteration). In this case, $R(Q)$ is the measure of an apparent rather than the true IESF (see appendix A).

4. Mean jump time and activation energy. — By analysing the shape of the various spectra, one can perform a more severe test of the model used and determine the mean jump time $\tau$. Moreover from the variation of the total intensity of the quasielastic spectra versus $Q$, one obtains information on the total amount of inelastic scattering, which reflects short time motions such as librations and vibrations. The latter is taken into account in the quasielastic region by multiplying the scattering law by a Debye-Waller factor $\exp(-Q^2 u^2)$ where $u^2$ is a mean square displacement. For the present case, we write the scattering law as (see appendix A)

$$S(Q, \omega) = \left[ \frac{P_l}{P_l} \delta(\omega) + \frac{P_m}{P_l} S_B(Q, \omega) \right] \exp(-Q^2 u^2).$$

(3)

Taking expression (A.5) with $P_l/P_l = 0.1$, which corresponds to 95 % deuteration of the phenyl rings (according to an NMR analysis, the deuteration was better than 93 %), we obtain the result shown in figure 2 (full line). The rather good agreement with the experimental data is a confirmation for model B.
We have compared this expression to the experimental data, using the fitting procedure described in reference [6]. First the data taken at 100°C, with an incident neutron wavelength of 8.25 Å were analysed. Expression (3) was fitted simultaneously to the spectra of eight scattering angles. Fixing $a = 1.032$ Å and $P_f/P_i = 0.1$ as previously, this leaves two fitting parameters except for a small background and a general scaling factor: the mean jump time $\tau$ and the mean square displacement $u^2$. The best values obtained from the fit are $\tau = 1.02 \times 10^{-11}$ s and $u^2 = 0.117 \text{Å}^2$. The theoretical spectra resulting from the fit are shown for four scattering angles in figure 3, together with the experimental points. The quality of the fit is an additional support for our model.

In order to study the temperature dependence of $\tau$, we have fitted expression (3) to the spectra obtained at 11 different temperatures between 17 and 117°C. In this calculation, the essential information is contained in the quasielastic line. The elastic peak was therefore excluded from the fitting procedure, thus eliminating its contribution to the statistical uncertainty introduced into the result due to the much higher elastic intensity. Examples of spectra obtained at four temperatures are shown in figure 4. Figure 5 shows that, in the temperature range of the present experiment, the obtained $\tau$ values follow an Arrhenius law

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (4)

with

$$\tau_0 = (0.35 \pm 0.07) \times 10^{-12} \text{ s}$$

and

$$E_a = 2.54 \pm 0.13 \text{ kcal/mole}.$$  

These results will be discussed in section 6.

5. Barrier to rotation of the methyl groups. — The aim of this section is to extract from the inelastic spectra, information about the potential barrier hindering the rotation of the methyl groups. Inelastic neutron scattering is a technique which is now widely used for such a purpose in a variety of systems containing methyl groups [12, 13]. In the present calculation, we follow a well known procedure [12], making the following usual assumptions.

a) The pronounced inelastic peak observed in PAA-OD4 near energy transfers of 31 meV (the peak position is independent of temperature within the experimental error) is mainly due to torsional oscillations of the methyl groups about their C3 axis. For our model picture, this assumption means that the
methyl groups are performing a librational motion during the average time \( r \) between two successive (instantaneous) \( C_3 \) rotational jumps. This will affect the spectrum in the quasielastic region only by a Debye-Waller factor, which was already included in the above calculations as part of the total Debye-Waller factor (eq. (3)). We note that such a large inelastic peak had already been observed in earlier neutron experiments [14] on solid PAA and was then attributed to hindered rotation of the \( CH_3 \) groups.

b) The partial Debye-Waller factor due to the librational motion alone in principle contains information on the hindering potential; however, it cannot be separated from the total effect of all short time motions. In addition, the value of the Debye-Waller factor is uncertain due to the effect of multiple scattering (see [18]). We assume that the methyl groups are moving in a threefold potential of the form

\[
V(\phi) = \frac{V_3}{2} (1 - \cos 3\phi).
\]

Since the methyl groups are attached to the rather heavy main body of the molecule bound in the crystal lattice we may neglect the coupling of methyl torsional oscillations to the other normal modes of the crystal. The torsional energy levels \( E_{uv} \) for this potential are characterized by a vibrational quantum number \( v \) and an index \( u \) which specifies the periodicity of the eigen-functions \( \psi_{uv} \). For a three-fold symmetric top \( \sigma = 0 \) or \( \pm 1 \) and the eigen-functions have A or E symmetry character respectively. The energy difference (expressed in frequency units) between A and E levels of the same vibrational quantum number \( v \), is called the tunnelling frequency. This energy difference is very small for the ground torsional level when the barrier \( V_3 \) is not too low (> 1 kcal/mole). In the following we therefore omit the subscript \( \sigma \). Tables have been produced [15], from which one can calculate the energy levels.

c) If we further assume that the inelastic peak seen in the neutron time-of-flight spectra of PAA-\( \theta \)D4 (near an energy transfer of 31 meV) is to a large extent due to the transition \( v = 1 \rightarrow v = 0 \), it is possible to extract the barrier height \( V_3 \). This assumption may be justified by comparison with the harmonic oscillator. A simple calculation of the scattering law for the latter shows that the main contribution to the scattered intensity in neutron energy gain comes indeed from this transition (see appendix B). We therefore set the difference of the two lowest energy levels \( E_1 - E_0 \) equal to the energy transfer at which the inelastic peak was observed in our experiment.

Let us now analyze the data using the above assumptions. The peak position in the inelastic region is rather well defined, as can be seen from figure 6. From the various spectra we estimated

\[
E_1 - E_0 = 31. \pm 1.5 \text{ meV}
\]

(250 ± 12 cm\(^{-1}\)) [16]. Then using relations (7) and the tables [15], we obtain the barrier height

\[
V_3 = 1.474 \pm 0.13 \text{ cm}\(^{-1}\) (4.21 ± 0.37 kcal/mole).
\]

This rather high barrier in turn justifies the comparison to the harmonic oscillator since the energy levels near the bottom of a deep potential well of the kind used here, indeed resemble those of a harmonic oscillator (the splitting of the ground energy level \( E_{0,0} - E_{0,\pm 1} \) (tunnelling splitting) is of the order of \( 10^{-6} \text{ cm}\(^{-1}\) and can therefore not be observed in our experiment).

6. Discussion. — The activation energy \( E_a \) deduced from the temperature dependence, between 17 and 117 °C, of the quasielastic scattering linewidth and the information on the potential barrier obtained independently from the position of a peak in the inelastic spectra, are in fact linked with one another. This fact may be used as a check on the data analysis and/or of the various assumptions made. The relation can be found from the following reasonable statement: the jump probability \( \tau^{-1} \) is proportional to the probability that the system is in an energy state \( E = V_3 \). For a thermally activated process, we should have:

\[
\tau^{-1} \propto Z^{-1} \exp[-(V_3 - E_0)/k_B T] \tag{6}
\]

with

\[
Z = \sum_{v=0}^\infty \exp[-(E_u - E_0)/k_B T] \tag{7}
\]

The right side of eq. (6) can in principle be calculated when the potential barrier is known [17]. If the model chosen for the potential is correct, the variation of expression (6) between \( T_1 \) and \( T_2 \) should reproduce
that of $\tau^{-1}$ deduced from the quasielastic width. In the present case, on an Arrhenius plot, this variation should be practically linear and the slope should be $E_a$. Using the cosine potential of eq. (5) with

$$V_3 = 1474 \pm 130 \text{ cm}^{-1},$$

the plot is indeed found to be linear within 4% but the slope, which by analogy may be considered as an activation energy, is $3.51 \pm 0.37$ kcal/mole, a value which is definitely greater than $E_a$ (see Fig. 5). Let us examine two possible reasons for such a discrepancy.

One possible reason is experimental. The neutron spectra were corrected for sample holder scattering, absorption and self-shielding, but not for multiple scattering. The latter correction might affect the widths of the quasielastic spectra in such a way that its temperature variation would change. We have therefore performed such a correction for two temperatures, 17 and 110 °C (these calculations are extremely time consuming), and applied the same fitting procedure to the spectra so corrected. As can be seen in figure 5, only very small changes in the $\tau$ values are obtained, showing that this possibility can be discarded [18]. Another possible reason is that eq. (6) may not be valid. Instead of considering only the energy $E = V_3$ one should perhaps take into account all the levels $E \geq V_3$. However, such a modification predicts a slope of the corresponding Arrhenius plot even greater than 3.51 kcal/mole. There are certainly other possibilities of improving eq. (6). However, we believe that one should try to explain the discrepancy by the choice of the potential used in the analysis. We chose the cosine form since it is widely used in the literature for similar problems [12]. It satisfies the symmetry condition, has a simple mathematical form and depends on only one adjustable parameter $V_3$, which is sufficient in many cases. In the present case, however, the experimental data provide two complementary sets of information contained in the quasielastic and inelastic regions of the neutron spectra, which in principle should permit a more precise determination of the potential shape. The result is that the true shape seems to deviate appreciably from the cosine form. The wells are probably narrower, leading to a greater value of the fundamental level $E_0$. An attempt to interpret the data in terms of such a potential will be presented elsewhere.

Another interesting result is the value of the pre-exponential factor in eq. (4). The physical meaning of this quantity deduced from Arrhenius plots is not always very clear. This problem is widely discussed in the literature [19], mainly in the classical picture. Here we limit the discussion to noting that, expressed in cm$^{-1}$ units, $\tau_0^{-1} = 15 \pm 3$ cm$^{-1}$. This value is much smaller than the angular frequency in each well $(E_1 - E_0 \approx 250$ cm$^{-1}$ (quantum picture) or $3(V_3/2 I)^{1/2} \approx 262$ cm$^{-1}$ (classical picture)), but of the same order of magnitude (within a factor 3) with the thermal free rotator angular frequency $(k_B T/12)^{1/2} \approx 50$ cm$^{-1}$, calculated in the middle of our temperature range $\approx 70$ °C.

7. Comparison with other data. --- Solid PAA has recently been studied by NMR [20]. Between 77 and 167 K it was found that the spin-lattice relaxation times $T_1$ and $T_1^p$ (in the laboratory and in the rotating frames) are dominated by the reorientation of the methyl groups. These authors estimate an activation energy of $\approx 3.2$ kcal/mole. If we determine for this temperature range the slope of an Arrhenius plot of expression (6) using, as before, a cosine potential with $V_3 = 1470$ cm$^{-1}$, we obtain an activation energy of 3.8 kcal/mole, which is definitely higher than the NMR value. Again this discrepancy might be explained by the failure of the cosine potential. It must be noted, however, that our activation energy value (2.54 kcal/mole) is not inconsistent with the NMR value, obtained in a lower temperature range. The reason for this is that whatever the potential shape, relation (6) predicts an activation energy, increasing with decreasing temperature. It is thus quite possible that NQES experiments between 77 and 167 K (but at much higher energy resolution) lead to an activation energy consistent with the NMR result, within experimental accuracy.

Results obtained from infrared, dielectric and neutron measurements by other authors [21] disagree with our data. They found a reorientational correlation time of $2.5 \times 10^{-11}$ s for the protons of the phenyl rings. This value is contradicted by our data on PAA-CD$_3$. A lower limit for this correlation time is given by our elastic energy resolution and is at least ten times larger. The same authors estimated a correlation time for methyl group rotation of $0.7 \times 10^{-12}$ s at 117°C, a value which is definitely too short (our result is $0.94 \times 10^{-11}$ s). In addition, we note that the broad low energy distribution observed in the neutron spectrum (Fig. 6 of ref. [21]) was resolved into two parts in our experiment: the above mentioned quasielastic line with a FWHM of 0.2 meV, and a low energy inelastic peak centered near an energy transfer of 2.5 meV, which has a width of about 1.6 meV FWHM. This peak appears for both PAA-OD4 and PAA-CD$_3$ at all temperatures at which we have studied these two substances. It therefore seems to be related to a motion of the whole molecule, possibly of torsional character. However, at this point we make no attempt to interpret this inelastic peak [22]. In figure 7 we show three examples of our data presented on a contracted energy scale such that this inelastic peak is seen. Note that due to the high energy resolution used in our experiment, this peak is about 20 times lower in amplitude than the quasielastic line, which in turn on this scale would be so narrow that it could hardly be seen. This is indicated by two dashed vertical parallel lines in
figure 7b. Note that the resolution (elastic line) is still narrower by a factor of about ten.

Finally, we wish to compare our data with recent far infrared and Raman spectra of anisole, more precisely the partially deuterated derivative C_{6}D_{5}—O—CH_{3} [23]. The authors observed weak absorption both in the gas and liquid phases, around 255 cm\(^{-1}\) (30.6 meV). This value is to be compared with the position of the inelastic peak (31. ± 1.5 meV) in our neutron spectra and strongly suggests that we are observing the same phenomenon, namely torsional vibrations of the CH\(_{3}\) of a methoxy group attached on a phenyl ring. This result shows also that in solid PAA the origin of the barrier to rotation is probably almost exclusively intramolecular. This is consistent with the geometry of the molecule since an O—CH\(_{3}\) group is smaller than a phenyl ring. As a consequence of this intramolecular character, it would be justified to extrapolate our present results on methyl rotation to the nematic and isotropic phases of PAA. This will probably be of importance in interpreting neutron data when other correlation times (e.g. for overall rotation and translation of the molecules) come in.

Acknowledgments. — We would like to thank Mrs. P. Baladda-Couturier and Miss P. Chenavas for their contribution in the synthesis of the samples, and are obliged to Dr. J. S. Higgins and Pr. G. Allen for useful discussions.

Appendix A. — In this appendix we derive the (quasielastic) scattering law for PAA-\(^{\text{OD}4}\) (eq. (3)). In addition to the incoherent scattering from the methyl protons, we have to take into account the incoherent contribution of the phenyl-deuterons (\(\sigma_{D} = 2.2\) barn) and of a small percentage \(z\) of protons remaining on the phenyl rings due to non perfect deuteration (\(\sigma_{H} = 79.7\) barn). The contribution of the other nuclei of the molecule is neglected. Since only the methyl groups are rotating, the contribution due to atoms of the phenyl groups will be a \(\delta(\omega)\) function. After these considerations, it is easily seen that the scattered neutron intensity from PAA-\(^{\text{OD}4}\) will be proportional to

\[
8[\sigma_{H} z + \sigma_{D}(1 - z)] \delta(\omega) + 6 \sigma_{H} S_{R}(Q, \omega) \tag{A.1}
\]

where \(S_{R}(Q, \omega)\) is given by (2a, b).

In order to obtain a normalized scattering law:

\[
\int_{-\infty}^{+\infty} S(Q, \omega) \, d\omega = 1 ,
\]

we define \(S(Q, \omega)\) by

\[
S(Q, \omega) = \frac{P_{f}}{ \frac{4}{3} z + \frac{4}{3} \sigma_{D} (1 - z)} + \frac{P_{m}}{ P_{f}} S_{R}(Q, \omega) \tag{A.2}
\]

with

\[
\frac{P_{f}}{ P_{f}} = \frac{4 z + 4 \sigma_{D} (1 - z)}{1 + 4 z + 4 \sigma_{D} (1 - z)} \tag{A.3}
\]

and

\[
P_{f} + P_{m} = P_{f} . \tag{A.4}
\]

\(P_{f}\) and \(P_{m}\) stand for the total number of fixed and rotating scattering centers expressed in units of \(\sigma_{H}\). Since these are fixed centers contributing to the elastic intensity, the coefficient \(A_{0}(Q)\) of the \(\delta(\omega)\) peak in the normalized scattering law is no longer the IESF of the rotational model, but may be defined as an apparent IESF connected with the true one \(A_{0}(Q)\) by the relation

\[
A_{0}(Q) = \frac{P_{f}}{ P_{f}} + \frac{P_{m}}{ P_{f}} A_{0}(Q) . \tag{A.5}
\]

Appendix B. — In this appendix, we calculate the contribution of different transitions of the torsional oscillator to the scattered intensity. Since the barrier to internal rotation of the methyl group is not too low, we may estimate the contributions of the different transitions to the scattered intensity by considering
the simpler case of the harmonic oscillator. In the limit of a very high barrier, the (three-fold degenerate) energy levels near the bottom of the well become the harmonic oscillator levels.

The scattering function for the harmonic oscillator is well known [24]:

\[
S(Q, \omega) = \exp \left[ -\frac{\hbar^2 Q^2}{2M^* \omega_0} \coth \left( \frac{\hbar \omega_0}{2k_B T} \right) \right] \times
\exp \left( \frac{\hbar \omega_0}{2k_B T} \right) \sum_{n=-\infty}^{+\infty} I_n(y) \delta(\hbar \omega - n\hbar \omega_0)
\]

with

\[
y = \frac{\hbar^2 Q^2}{2M^*} \left( \frac{\hbar \omega_0}{2k_B T} \right)^{-1}
\]

\(M^*\) is the effective mass for a methyl group (three times the mass \(M\) of a proton).

For the spectra shown in figure 1, we have \(T = 373\, \text{K}\), \(Q = 4.3\, \text{Å}^{-1}\) at \(\hbar \omega_0 = 31\, \text{meV}\); calculating the argument of the Bessel function one obtains:

\[y = 0.875\, 5\, 5\, \text{.}\]

The neutron energy gain lines correspond to \(n < 0\). It is easily verified that the \(n = -1\) line accounts for 88% of the inelastically scattered intensity.

References and footnotes

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[7] HERVET, H., VOLINO, F., DIANOUX, A. J. and LECHNER, R. E., 

[8] Throughout this paper we are using alternatively three different 
energy units each of which is customary in laboratories 
using different techniques. For convenience we give here 
the relationship between these units:

\[1\, \text{meV} = 0.00855\, 73\, \text{cm}^{-1} = 0.023, 061\, \text{kcal/mole}.

[9] JANIK, J. A., JANIK, J. M., NGUYEN THI THOA, RUNIAWSKI, 
(1971) 1068.
(1975) 1181; see appendix (A.8).
[12] See, for example, Internal Rotation in Molecules, edited by 
W. J. Orville-Thomas (John Wiley) 1974, especially 
Chapter 7, p. 217, by CUNLIFFE, A. V. and Chapter 8, 
p. 255 by ALLEN, G. and FEWSTER, S.
157.
MÖLLER, K. D., DE MEIO, A. R., SMITH, D. R. and LONDON, 
[16] In fact, this peak completely disappears from the spectra when 
plotting on an energy scale. However, it has been shown 
(see e.g., BRIER, P. N., HIGGINS, J. S. and BRADLEY, R. H. 
Mol. Phys. 21 (1971) 721) that the relevant quantity for 
the assignment of peaks is the generalized frequency 
function \(\rho(\omega)\) rather than the scattering function \(S(Q, \omega)\). We have

\[
\rho(\omega) = \omega^2 \lim_{Q^2 \to \omega} \left[ \frac{S(Q, \omega)}{Q^2} \exp \left( \frac{\hbar \omega}{2k_B T} \right) \right].
\]

If, for large \(\omega\) (\(\hbar \omega \gg \epsilon_0\), where \(\epsilon_0\) is the incident neutron 
energy), the shape of the scattering function is independent 
of \(Q\), the time of flight spectrum reproduces the function 
\(\rho(\omega)\). In our TOF-spectra, we have verified that, to 
experimental accuracy, the peak position is independent 
of the scattering angle (the \(Q\) value at the inelastic peak 
position varies from 3 to 5 \(\text{Å}^{-1}\) with the angle) and in 
dependent of temperature (although it slightly broadens 
with increasing temperature). We assume that this remains 
true down to \(Q^2 \to 0\). We have also verified that the 
functions \(\omega^2/Q^2 S(Q, \omega) \exp(\hbar \omega/2k_BT)\) is peaked 
ly at the same position as the TOF spectra and has the 
same properties.

[17] In fact, at very low temperature we have

\[
\tau^{-1} \propto \exp[-(V_3 - \epsilon_0)/k_B T]
\]

so that the activation energy \(E_a\) is given by \(V_3 - \epsilon_0\).

This expression has been used by other authors for similar 
problems [ALLEN, P. S. and SNELL, A. J., J. Phys. C : 

[18] This result is consistent with previous calculations for similar 
experimental conditions [7], where it has been shown that 
both the IESF and mean jump time are slightly affected 
(a few per cent) by multiple scattering. On the other hand, 
the mean square displacement \(\langle u^2\rangle\) is probably increased 
by a factor of 1.5 to 2 as compared to the true value. For 
the calculation, we used the same multiple scattering 
approximation as in reference [7].

[22] In this context it should be mentioned that — contrary to 
observations made by other authors [3] using fully deute-
rated samples of PAA — we have not observed an appreci-
able increase of the intensity anywhere in our spectra, 
when approaching the solid to nematic phase transition. 
But this is perhaps not surprising, since in our case most 
of the scattering was incoherent.

[23] FEWSTER, S., Ph. D. Thesis, University of Manchester (1970); 
see also reference [12], p. 275.
[24] MARSHALL, W. and LOVESY, S. W., Theory of Thermal 