

Structure Factors for Neutron Scattering on Tunnelling Methyl Groups in Nitromethane

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Received September 2, 1982

The elastic, quasielastic and inelastic structure factors for neutron scattering on CH_3 groups tunnelling in a sinusoidal hindering potential with threefold symmetry are calculated as a function of the momentum transfer Q . A comparison is made with data on methyl groups in nitromethane obtained with high resolution inelastic neutron scattering experiments at high momentum transfer.

1. Introduction

Rotational tunnelling of small molecules or molecular groups like CH_4 , NH_4^+ and CH_3 has been studied extensively in recent years with spectroscopic methods like N.M.R. and high resolution inelastic neutron scattering [1]. Several papers were published about the theory of neutron scattering cross sections: Hüller [2] treated the case of a tetrahedron like CH_4 or NH_4^+ in a three dimensional potential with high barriers to rotation, i.e. $V \gg B$ where $B = \hbar^2/2I$ is the rotational constant with the moment of inertia I . The basis of this theory is the pocket state formalism. The pocket states were approximated by delta functions in the equilibrium orientation. Therefore this approach is valid for cases with rather high barriers and low momentum transfer $Q \ll 1/R$ where R is the radius of the molecule ($R = 1.08 \text{ \AA}$ for a CH_3 group).

Ozaki et al [3] improved these calculations for the special case of CH_4 in phase II employing a series expansion into free rotor states on the basis of the extended James-Keenan model [4]. Hüller and Press [5] extended Hüller's [2] calculations abandoning the delta function approximation and allowing for a finite width of the pocket states.

The calculation of the scattering cross sections of a tunnelling methyl group which behaves like a *one*

dimensional rotator has been performed by Hüller [6] with the delta function approximation. Clough et al. [7] improved the calculation employing spatial wavefunctions which were obtained by solving the Schrödinger equation of the CH_3 group in a sinusoidal potential with three and sixfold symmetry. Due to the approximations made the results are however only valid for small momentum transfer $Q < 1/R$.

We have extended these calculations to the case of large $Q \cdot R$. In Sect. 2 we derive the expressions for the neutron scattering cross sections. The results are compared in Sect. 3 with experimental data obtained on nitromethane with the new backscattering spectrometer IN13 at the HFR in Grenoble.

2. Neutron Scattering Cross Sections

We use the notations as introduced by Hüller [2] and Clough [7]. The Hamiltonian H_{NM} describes the spin-dependent interaction between the neutron and the three protons of the methyl group:

$$H_{NM} = \frac{2a_{\text{inc}}}{\sqrt{I(I+1)}} \sum_{k=1}^3 \delta(\mathbf{r} - \mathbf{R}_k) \mathbf{s} \cdot \mathbf{I}^k \quad (1)$$

\mathbf{R}_K is the position of the K -th proton, \mathbf{I}^K its spin operator. \mathbf{s} and \mathbf{r} are the spin and position of the neutron. a_{inc} is the spin-dependent scattering length of the proton. Equation (1) can be symmetry adapted [7]:

$$H_{NM} = H_{NM}^A + H_{NM}^{E^a} + H_{NM}^{E^b} \quad (2)$$

with

$$H_{NM}^A = \frac{1}{3} [\delta(\mathbf{r} - \mathbf{R}_1) + \delta(\mathbf{r} - \mathbf{R}_2) + \delta(\mathbf{r} - \mathbf{R}_3)] \cdot \mathbf{s} \cdot (\mathbf{I}^1 + \mathbf{I}^2 + \mathbf{I}^3)$$

and

$$H_{NM}^{E^a} = \frac{1}{3} [\delta(\mathbf{r} - \mathbf{R}_1) + \varepsilon \delta(\mathbf{r} - \mathbf{R}_2) + \varepsilon^* \delta(\mathbf{r} - \mathbf{R}_3)] \cdot \mathbf{s} \cdot (\mathbf{I}^1 + \varepsilon^* \mathbf{I}^2 + \varepsilon \mathbf{I}^3)$$

where $\varepsilon = \exp(2\pi i/3)$.

$H_{NM}^{E^b}$ is the Hermitian conjugate of $H_{NM}^{E^a}$.

The double differential neutron scattering cross section can be written as [2]:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k} \sum_{\mu\mu'} \sum_{aa'} P_\mu P_a |\langle \Psi_a' | \langle \mu' \mathbf{k} | H_{NM} | \mu \mathbf{k} \rangle | \Psi_a \rangle|^2 \cdot \delta(\omega - \omega_{aa'}). \quad (3)$$

Unprimed symbols relate to quantities before the scattering event, primed symbols to those after scattering. Ω is the solid angle and $\hbar\omega$ the energy transfer. $|\mu \mathbf{k}\rangle$ is the wavefunction of the neutron:

$$|\mu \mathbf{k}\rangle = |\mu\rangle e^{i\mathbf{k} \cdot \mathbf{r}}$$

where $|\mu\rangle$ is the spin state. P_μ and P_a are the initial probabilities for $|\mu\rangle$ and the state $|\Psi_a\rangle$ of the target with the energy E_a .

If one assumes that the methyl group is rigid then the neutron scattering operators

$H_M^X \equiv \langle \mu' \mathbf{k}' | H_{NM}^X | \mu \mathbf{k} \rangle$ with $X = A, E^a, E^b$ have the following form

$$H_M^X = (H_M^X)_{\text{spin}} (H_M^X)_{\text{space}} \quad (4)$$

with

$$(H_M^A)_{\text{spin}} = \mathbf{s} \cdot (\mathbf{I}^1 + \mathbf{I}^2 + \mathbf{I}^3) \quad (5)$$

$$(H_M^{E^a})_{\text{spin}} = \mathbf{s} \cdot (\mathbf{I}^1 + \varepsilon^* \mathbf{I}^2 + \varepsilon \mathbf{I}^3)$$

and

$$(H_M^A)_{\text{space}} = \frac{1}{3} [\exp(ix \cos \phi) + \exp(ix \cos(\phi - 2\pi/3)) + \exp(ix \cos(\phi + 2\pi/3))] \quad (6)$$

$$(H_M^{E^a})_{\text{space}} = \frac{1}{3} [\exp(ix \cos \phi) + \varepsilon \exp(ix \cos(\phi - 2\pi/3)) + \varepsilon^* \exp(ix \cos(\phi + 2\pi/3))]$$

ϕ is the coordinate describing the motion of the methyl group and $x = QR \sin \theta$ where θ is the angle

between \mathbf{Q} and the rotation axis of the group. The matrix elements of the spin part of H_M^X are \mathbf{Q} independent [7].

In order to calculate the matrix elements of the spatial part, we expand the wavefunctions $|\Psi_a\rangle$ into a series of free rotor states, i.e.:

$$|\Psi_a\rangle = \sum_m a_m \exp(im(\phi - \phi_0)) \quad (7)$$

Thus the matrix elements H_{space}^X for a transition between states $|\Psi_a\rangle$ and $|\Psi_a'\rangle$ can be written as:

$$H_{\text{space}}^X = \sum_{n,m} a_n a_m' \int_{-\pi}^{+\pi} (H_M^X)_{\text{space}} \exp(i(m-n)(\phi - \phi_0)) d\phi \quad (8)$$

Putting $m - n = r$ one obtains:

$$H_{\text{space}}^X = 2\pi \sum_r \sum_n a_n a_{n+r}' F_r^X J_r(x) e^{-ir\phi_0} \quad (9)$$

where $J_r(x)$ is the Bessel function of the first kind of order r and

$$F_r^{E^a, E^b, A} = \begin{cases} 0 & \text{if } (r-1) \bmod 3 \neq 0, (r+1) \bmod 3 \neq 0, \\ r \bmod 3 \neq 0 \\ r' & \text{if } (r-1) \bmod 3 = 0, (r+1) \bmod 3 = 0, \\ r \bmod 3 = 0 \end{cases} \quad (10)$$

Inserting (9) into (3) yields the elastic (for $X=A$), quasielastic and inelastic (for $X=E^a, E^b$) neutron scattering cross sections for transitions between energy levels with wave functions $|\Psi_a\rangle$ and $|\Psi_a'\rangle$ for the case of a single crystalline sample with CH_3 groups of equal orientation.

For a polycrystalline sample a powder average over ϕ_0 and θ has to be performed. The average over ϕ_0 yields:

$$\overline{|\langle \Psi_a' | H^X | \Psi_a \rangle|^2}^{\phi_0} = \sum_r (c_r^X)^2 J_r^2(x) \quad (11)$$

with

$$(C_r^{E^a, E^b})_{aa'} = \begin{cases} 0 & r \bmod 3 = 0 \\ \sum_m a_m a_{m\pm r}' & r \bmod 3 = 1 \\ \sum_m a_m a_{m\mp r}' & r \bmod 3 = -1 \end{cases} \quad (12)$$

and

$$(C_r^A)_{aa'} = \begin{cases} \sum_m (a_m a_{m+r}' + a_{m+r} a_m') & r \bmod 3 = 0 \\ \sum_m a_m a_m' & r = 0 \\ 0 & r \bmod 3 = \pm 1 \end{cases} \quad (13)$$

From the average over ϕ_0 and θ we obtain:

$$\overline{|\langle \Psi_a | H^X | \Psi_a \rangle|^2}^{\phi_0, \theta} = \sum_r (C_r^X)^2 \frac{1}{2QR} \int_0^{2QR} J_{2r}(t) dt \quad (14)$$

The coefficients $(C_r^X)_{aa}$ can be calculated by numerical integration of the Schrödinger equation with the Hamiltonian

$$H = B \left(-\frac{\partial^2}{\partial \phi^2} + V(\phi) \right) \quad (15)$$

with

$$B = \frac{\hbar^2}{2I} = 593 \mu\text{eV}$$

and

$$V(\phi) = \sum_{n=1}^N V_{3n} \cos(3n\phi). \quad (16)$$

The coefficients V_{3n} represent the strength of the hindering potential. They are scaled to the rotational constant B .

The elastic, quasielastic ($E^a \leftrightarrow E^b$) and inelastic ($A \leftrightarrow E^a, E^b$) structure factors for transitions between levels of the molecular groundstate are plotted in Fig. 1a, b, c as a function of Q with the barrier height as parameter. The continuous line corresponds to the case of nitromethane (tunnel splitting $35 \mu\text{eV}$ [8]) assuming a purely 3-fold cosine potential with $V_3/B=16$. The dotted curves are valid for the free rotor, the dashed for very high barriers. It turns out that for the latter case the structure factors are the same as those obtained by the delta function approximation. It is interesting to note that the quasi-elastic and inelastic structure factors are very different for the case of the free rotor, but they become quickly identical with increasing barrier height V_3 . The quasielastic structure factor for the case of a purely sixfold potential stays however rather close to the one of the free rotor, independent of the barrier height.

The sum S of all structure factors of transitions between levels of the ground state i.e. the intensity of elastically or “nearly” elastically scattered neutrons is plotted on a logarithmic scale as a function of Q^2 in Fig. 2. Obviously the Q -dependence resembles to that of a Debye Waller factor $\exp(-x^2 Q^2)$ if the barrier height is sufficiently high ($V_3 > 15$). In this case x^2 is in a first order approximation proportional to the mean square amplitude of “libration” $\langle u^2 \rangle_{\text{lib}}$:

$$x^2 = \frac{1}{3} \langle u^2 \rangle_{\text{lib}}$$

The factor $1/3$ occurs due to the fact that the libration of a CH_3 group has only *one* degree of free-

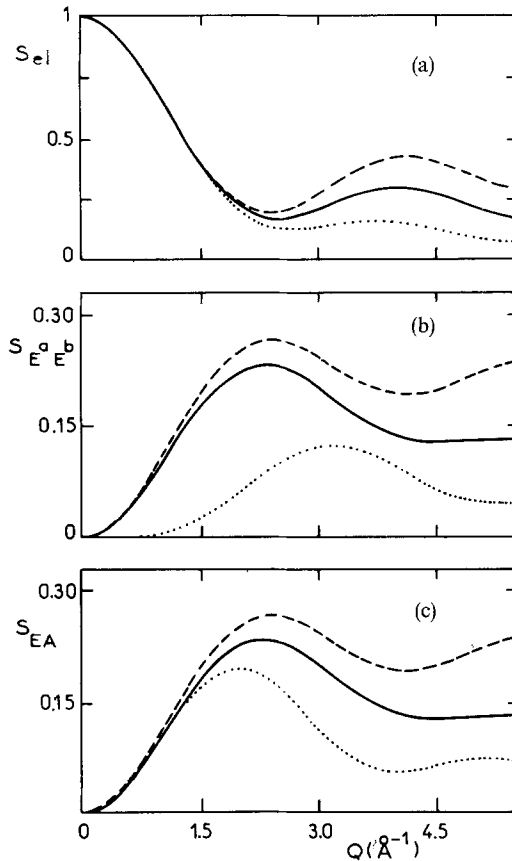


Fig. 1. Calculated elastic (a), quasielastic (b) and inelastic (c) structure factors of methyl groups in a polycrystal as a function of the momentum transfer Q for three different barrier heights V_3 with $V_6=0$. --- $V_3 = \infty$, — $V_3 = 16B$, $V_3 = 0$

dom. For nitromethane ($V_3/B=16$) we obtain $\langle u^2 \rangle_{\text{lib}} = 0.06 \text{ \AA}^2$ corresponding to a “librational” amplitude of 13° .

If one divides all structure factors for transitions in the groundstate by the Debye Waller factor then the Q dependence of these renormalized structure factors is practically identical with those valid for very high barriers. Therefore it is legitimate for values $V_3 > 15$ to approximate the structure factors by a product of a Debye Waller factor and the structure factor for the delta function case i.e.:

$$S_{\text{el}} = \exp(-\frac{1}{3} \langle u^2 \rangle_{\text{lib}} Q^2) \cdot \frac{1}{3} (1 + 2j_0(QD)) \quad (17)$$

$$S_{A, E} = S_{E_a, E_b} = \exp(-\frac{1}{3} \langle u^2 \rangle_{\text{lib}} Q^2) \cdot \frac{2}{9} (1 - j_0(QD)). \quad (18)$$

Where $j_0(x)$ is the spherical Bessel function of order zero and D the proton-proton distance. The error introduced is always less than 3%.

The Q dependence of the structure factors for transitions between the groundstate and the first excited state i.e. librational excitations is plotted in Fig. 3

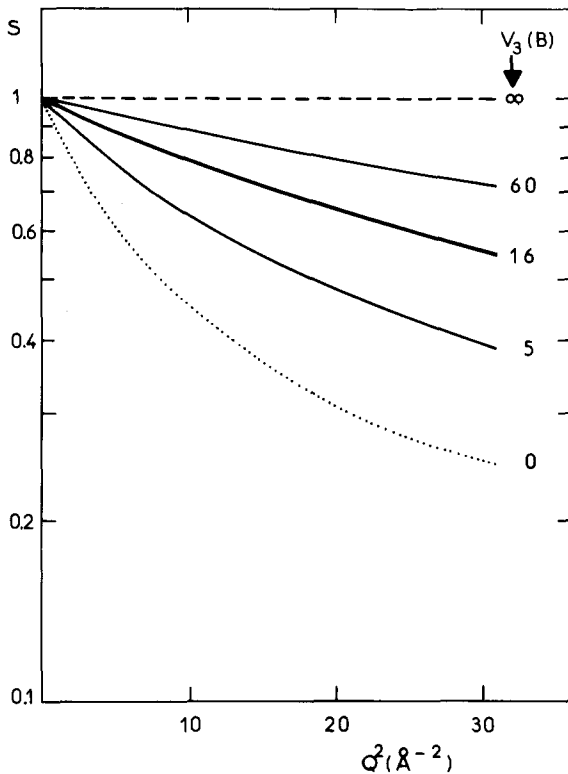


Fig. 2. Calculated sum S of all structure factors of transitions between levels of the groundstate on a logarithmic scale as a function of Q^2 for various barrier heights V_3 with $V_6=0$

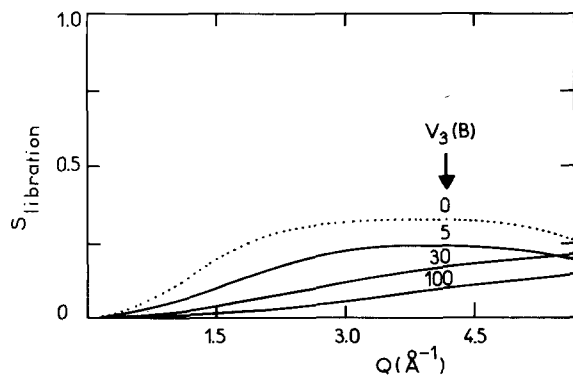


Fig. 3. Calculated Q dependence of the structure factors for transitions between the groundstate and the first excited librational state

for various barrier heights. At small Q , a Q^2 dependence is observed as expected for a harmonic oscillator.

It is interesting to note that the elastic incoherent structure factor (EISF) [9] valid for a stochastically reorienting methyl group is identical with the one of a tunnelling CH_3 group provided that both cases are taken under equivalent conditions. For example: Rotational diffusion equivalent to free rotation, or

jump reorientation between three completely localised orientations equivalent to tunnelling through very high barriers. The EISF for the case of an uniaxial rotator reorientating stochastically in a N -fold cosine potential has been calculated by Dianoux and Volino [10]. Again their EISF valid for a methyl group is identical with the one derived in this paper (14) for the quantum mechanical case. The frequency dependence of the classical case is however completely different from the quantum mechanical case. In the former quasielastic scattering is observed, in the latter inelastic scattering due to the periodic character of the tunnelling and librational motion.

3. Experimental Details and Analysis

The sample investigated was nitromethane (NO_2CH_3) which is liquid at room temperature. It was poured into a thinwalled sample container made of aluminium yielding a specimen with the shape of a hollow cylinder with a radius of 15 mm, a thickness of 0.3 mm and a height of 30 mm. A transmission of 0.85 was measured for a 2 \AA neutron beam passing through the center of the sample. The sample was cooled down to 5 K in a helium cryostat with a temperature stability of 0.2 K. The experiments were performed at the high flux reactor of the Institute Laue-Langevin using the new backscattering spectrometer IN13 for thermal neutrons [11]. The incident energy was 16.3 meV, the energy resolution $8 \mu\text{eV}$ (FWHM). A Q -range from 1.4 to 5.4 \AA^{-1} was covered. Spectra at 15 different Q -values were recorded, 11 of them simultaneously with a typical beam time between 12 and 24 h. The data was treated in the usual way: After subtraction of the empty cell data the spectra were normalized with a calibration run performed with a vanadium standard whose dimensions were identical to those of the sample except the thickness which was 2.5 mm. Cylinder corrections were applied to eliminate the influence of self-shielding and absorption. The normalization was done in such a way that the integral of the spectra from $\hbar\omega = -\infty$ to $+\infty$ is one. The data were in addition corrected for multiple scattering [12]. These corrections are rather small (1 to 5%) in the Q range we investigated. They become large (10 to 50%) at Q values smaller than 1 \AA^{-1} .

A typical spectrum is shown in Fig. 4. The continuous line represents a fit with a sum of two resolution curves yielding a tunnel splitting of $35 \mu\text{eV}$ in agreement with the value published recently [8]. The elastic and inelastic integrated intensities J'_{e1} and J_{EA} were obtained by numerical

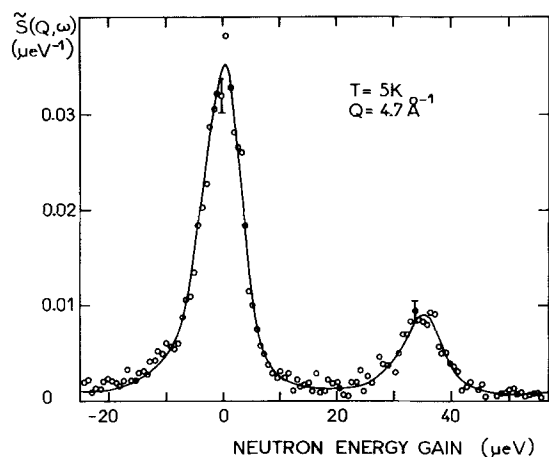


Fig. 4. Energy spectrum of neutrons scattered in NO_2CH_3 at 5 K. Momentum transfer $Q = 4.7 \text{ \AA}^{-1}$

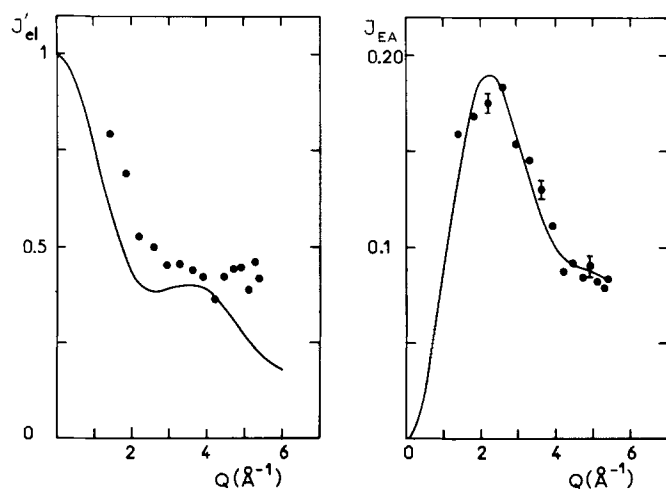


Fig. 5. Experimental results for the Q dependence of the "elastic" and inelastic integrated intensities of CH_3 groups in NO_2CH_3 . The continuous curve corresponds to a fit as explained in the text

integration of the data after subtraction of a constant background. These integrals are proportional to the "elastic" and inelastic structure factors S'_{el} and S_{EA} , the proportionality constant being the Debye Waller factor $\exp(-\langle u^2 \rangle_{vib} Q^2)$ for the center of mass vibration of the group. Remember that S'_{el} contains the sum of the truly elastic and the quasielastic structure factors S_{el} and $S_{EA}E_b$. Figure 5 shows these integrals as a function of the momentum transfer Q .

The Q dependence of the inelastic integral J_{EA} was then fitted with (18) multiplied with a weight factor W and a temperature factor $2/(1 + e^{\hbar\omega_i/k_B T})$ which takes detailed balance into account i.e. we assume that the CH_3 groups were in thermal equilibrium

with the phonon bath. The mean square amplitude $\langle u^2 \rangle = \frac{1}{3} \langle u^2 \rangle_{lib} + \langle u^2 \rangle_{vib}$ and W were taken as fit parameters.

The use of a weight factor W which is theoretically equal to one can be justified by the facts that neither the number of tunnelling CH_3 groups present in the sample is known precisely nor the corrections applied are perfect. The continuous lines in Fig. 5 show the fit result with

$$\langle u^2 \rangle = 0.029 \pm 0.002 \text{ \AA}^2$$

$$W = 0.85 \pm 0.02.$$

Apparently the fit is quite good. The experimental values of the integral J'_{el} are however always higher than those calculated with the above given parameters. This discrepancy can be explained by the fact that coherent elastic scattering from Bragg peaks of the sample could not be eliminated in the experiment. Therefore the experimental values of J'_{el} don't carry quantitative information.

The fitted value of W of 0.85 is rather near to one showing that the normalization procedure worked quite well. The mean square amplitude $\langle u^2 \rangle$ contains the sum of the librational and vibrational part. As outlined in section 1 we can calculate $\langle u^2 \rangle_{lib}$. For NO_2CH_3 we obtain $\langle u^2 \rangle_{lib} = 0.06 \text{ \AA}^2$ if we use a purely three fold cosine potential which is a reasonable assumption [8]. Therefore we deduce a value for $\langle u^2 \rangle_{vib} = 0.009 \pm 0.003 \text{ \AA}^2$.

Trevino et al. [13] determined the ellipsoid $\langle u^2 \rangle_{ij}$ of the thermal clouds of the deuterons in fully deuterated nitromethane from a neutron diffraction experiment. The value for $\langle u^2 \rangle$ extracted from our experiment can be related to $\langle u^2 \rangle_{ij}$ by the expression:

$$\langle u^2 \rangle = \frac{1}{3} \sum_{i=1}^3 \langle u^2 \rangle_{ii} \quad (19)$$

yielding $\langle u^2 \rangle = 0.028 \pm 0.0003 \text{ \AA}^2$ at 4 K in agreement with our result which is however valid for protons. In order to calculate $\langle u^2 \rangle_{lib}$ for CD_3 groups in nitromethane we have to double the scaled potential V_3 compared to the case of protonated groups. We obtain

$$\langle u^2 \rangle_{lib}^{\text{deuteron}} = 0.04 \text{ \AA}^2.$$

This corresponds to a librational amplitude of 10.7° .

As we do not expect a significant difference of $\langle u^2 \rangle_{vib}$ for the two isotopic species we estimate:

$$\langle u^2 \rangle^{\text{deuteron}} = \frac{0.04}{3} + 0.009 = 0.023 \pm 0.003 \text{ \AA}^2.$$

This value is about 20% smaller than the one found by Trevino et al. [13]. The difference is twice as large as the statistical error, i.e. not really significant yet.

4. Conclusion

We have measured the inelastic structure factor of a tunnelling methyl group by high resolution inelastic neutron scattering at high momentum transfer. The results are in good agreement with theoretical calculations and with neutron diffraction data.

References

1. Press, W.: Springer Tracts in Modern Physics. Vol. 92. Berlin, Heidelberg, New York: Springer (1981)
2. Hüller, A.: Phys. Rev. B **16**, 1844 (1977)
3. Ozaki, Y., Kataoka, Y., Yamamoto, T.: J. Chem. Phys. **73**, 3442 (1980)
4. James, H.M., Keenan, T.A.: J. Chem. Phys. **31**, 12 (1959)
5. Hüller, A., Press, W.: Phys. Rev. B **24**, 17 (1981)
6. Hüller, A.: (unpublished)
7. Clough, S., Heidemann, A., Paley, M.: J. Phys. C: Solid State Phys. **13**, 4009 (1980)
8. Alefeld, B., Anderson, I.S., Heidemann, A., Magerl, A., Trevino, S.: J. Chem. Phys. **76**, 2758 (1982)
9. Lechner, R.E., Heidemann, A.: Commun. Phys. **1**, 213 (1976)
10. Dianoux, A.J., Volino, F.: Mol. Phys. **34**, 1263 (1977)
11. Maier, B.: Neutron beam facilities. Available for users. Ed. 1981, copies can be obtained from B. Maier, ILL, 156X, F-38042 Grenoble, Cedex, France
12. Johnson, M.W.: Computer program DISCUS, Harwell Report HL74/1054 (13) (1974)
13. Trevino, S.F., Prince, E., Hubbard, C.R.: J. Chem. Phys. **73**, 2996 (1980)

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