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ИССЛЕДОВАНИЙ  
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P.S.Goyal, I.Natkaniec, W.Nawrocik,  
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STUDY OF UNIAXIAL  
MOLECULAR REORIENTATIONS  
BY COLD NEUTRON SCATTERING

**1973**

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**STUDY OF UNIAXIAL  
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BY COLD NEUTRON SCATTERING**

Объединенный институт  
ядерных исследований  
БИБЛИОТЕКА

Гойал П.С., Натканец И., Навроцик В., Домославски Я. E14 - 7648

Исследование одноосевой реориентации молекул методом  
неупругого рассеяния нейтронов

Получены формулы для сечения квазиупругого рассеяния нейтронов в случае ротационной диффузии молекул вокруг фиксированной оси. На основе численных расчетов, проведенных для трех величин углового скачка молекулы, показано, что метод квазиупругого рассеяния нейтронов может быть применен для определения временных и геометрических параметров реориентации молекул в пластических кристаллах.

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Goyal P.S., Natkaniec I., Nawrocik W.,  
Domoslawski J. E14 - 7648

Study of Uniaxial Molecular Reorientations  
by Cold Neutron Scattering

The expression for the cross-section of neutron quasielastic scattering from a molecule, reorienting about a fixed axis has been derived. Three possibilities for the angular jump lengths are discussed and it is shown that neutron quasielastic scattering technique can be used for investigating the rate and geometry of reorientations in molecular crystals.

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Dubna, 1973

I. Introduction

Inelastic neutron scattering is a powerful tool in studying the rotational motions of molecules in the time range  $10^{-13}$  -  $10^{-11}$  sec and space range  $0.1$  -  $10$  Å. For the explanation of the results from neutron scattering experiments an extensive use has been made of simplifying models for the dynamics of molecules. Reviews of these have been given by Janik /1/, Springer /2/ and Dahlborg et al./3/. If a monoenergetic neutron interacts with a molecule tightly bound in a crystal, the energy spectrum of scattered neutrons consists of two parts. An inelastic contribution is due to interaction of neutrons with vibrations (translational and librational) of molecules and a sharp elastic line at zero energy transfer. If these molecules possess other degrees of freedom which undergo random rather than oscillatory motions, they give rise to broadening of the elastic line and are often called "quasielastic". Molecular reorientations in plastic phase of some molecular crystals are the

example of such random reorientations. By investigating incoherent quasielastic scattering from hydrogenous plastic solids one can draw a conclusion on the rate and geometry of reorientational motions/4,5, 6,7,8/. In many cases because of steric reasons the reorientations are restricted to those about a fixed axis. In the present communication we report the derivation of neutron scattering cross-section for such a molecule which is reorienting about a fixed axis. The model assumes instantaneous reorientational jumps. Molecular reorientations through an angle of 30°, 60° and 120° are considered.

## II. Derivation of scattering law

Van Hove /9/ has shown that the incoherent differential scattering cross-section per atom per unit solid angle and per unit energy interval is given by:

$$\frac{d^2 \delta_{inc}}{d\Omega dE} /_{atom} = a_{inc}^2 \frac{1}{h} \frac{k}{k_0} e^{\frac{-\hbar\omega}{2k_B T}} S(\vec{k}, \omega) \dots /1/$$

$$S(\vec{k}, \omega) = \frac{1}{2\pi} \int G_S(\vec{r}, t) e^{i(\vec{k} \cdot \vec{r} - \omega t)} d\vec{r} dt \dots /2/$$

where  $\hbar \vec{k} = \hbar (\vec{k}_0 - \vec{k})$

$$\mathcal{E} = \hbar \omega = E_0 - E = \frac{\hbar^2}{2m} (k_0^2 - k^2)$$

are momentum and energy transfer during scattering processes,  $k_0$ ,  $E_0$  and  $k, E$  are the wave vector and the energy of incident and scattered neutrons respectively,  $T$  is the temperature of the scatterer,  $m$ ,  $k_B$ ,  $\hbar$  are the mass of neutron, Boltzman constant and Planck constant respectively. Here  $G_S(\vec{r}, t)$  is the classical self correlation function. If a particle is at the origin at time  $t=0$ ,  $G_S(\vec{r}, t)$  gives the probability of finding that a particle at  $\vec{r}$  after time  $t$  has elapsed.

The expression for  $G_S(\vec{r}, t)$  can be easily written when a molecule is making frequent rotational jumps between a finite number of equilibrium orientations. Let us consider a hydrogenous molecule reorienting about a fixed axis. Incoherent scattering will be mainly from protons. In the present derivation we consider scattering from a single proton. The total incoherent scattering from a molecule can be obtained by simple addition of contributions from various protons in the molecule. A reorientation of a molecule is equivalent to the motion of proton to another equivalent site on a ring around the axis about which the molecule is reorienting. Various protons in the molecule may be moving on rings of different radii, depending on the structure of the molecule. If the molecule reorients through an angle of  $\theta$ ,  $\frac{2\pi}{\theta}$  are the number of equilibrium sites for proton on the circumference of ring. When the molecule is in one of its equilibrium orientations, the proton performs various types of vibrations around its equilibrium position. In the present formulation we assume that vibrations and reorientations are independent and that only the part of motion of protons which is due to reorientations give rise to quasielastic scattering. The vibratory motions will result in a Debye-Waller factor. We also assume that the reorientation time is negligibly small compared to the time  $\tau$  between successive reorientations; so that the proton is always at one of the equilibrium positions. So the self correlation function for the proton can be written as

$$G_S(\vec{r}, t) = \sum_{i=1}^N P_i(t) \delta(\vec{r} - \vec{r}_i) \dots /3/$$

where the summation is done over all possible equilibrium sites for the proton.  $\vec{r}_i$  gives the position of these sites on the circumference of a ring.  $P_i(t)$  is the probability of finding proton at  $i$ -th site if it was at origin at  $t = 0$ .

If the jumps are allowed only to the nearest neighbouring site and we assume that a clockwise and anticlockwise reorientations are equally probable, then  $P_i(t)$  is given /10/ by a differential equation:

$$\frac{dP_i(t)}{dt} = \frac{1}{2\tau} [P_{i+1}(t) + P_{i-1}(t)] - \frac{P_i(t)}{\tau} \quad /4/$$

One can choose origin at the first site from where proton starts. At any time  $t$  the proton should be sitting at one of the equilibrium positions. But after a very long time, it will appear to be equally distributed over these sites. Thus  $P_i(t)$  should satisfy the following boundary conditions:

$$P_1(0) = 1, \quad \sum_{i=1}^N P_i(t) = 1, \quad P_i(\infty) = \frac{1}{N}.$$

We considered three possibilities when the molecule reorients through an angle of  $120^\circ$ ,  $60^\circ$  and  $30^\circ$  respectively. The number of coupled differential equations in three cases was different but the solution could always be expressed in the following form /11/

$$P_i(t) = \frac{1}{N} \sum_{k=1}^n a_{ik} e^{-b_k \frac{t}{\tau}} \quad \dots \quad /5/$$

where  $n = 2, 4$  and  $7$  for  $120^\circ, 60^\circ$  and  $30^\circ$  jumps respectively. The values of  $a_{ik}$  and  $b_k$  are given in Table I for the three cases under consideration. These expressions for probability functions are substituted in equation /2/ and their Fourier transform over space and time is evaluated. It is then averaged over initial sites to obtain the scattering law. If the sample is polycrystalline, the scattering law should be further averaged over all directions of  $\vec{K}$ . The scattering law for polycrystalline substances for the three cases under discussion can be expressed as follows:

Case I Reorientational jump by  $120^\circ$

$$S(K, \varepsilon) \sim \pi \left(1 + \frac{2 \sin KR}{KR}\right) \delta(\varepsilon) + 2 \left(1 - \frac{\sin KR}{KR}\right) L(\Gamma, \varepsilon),$$

where

$$L(\Gamma, \varepsilon) = \frac{\Gamma}{\Gamma^2 + \varepsilon^2} \quad \text{and} \quad \Gamma = \frac{3}{2} \frac{h}{\tau}$$

$$R = 2d \sin \frac{\pi}{3}$$

Here  $d$  is the radius of the circle on the circumference of which the proton is moving.

Case II: Reorientational jumps by  $60^\circ$

$$S(K, \varepsilon) = \pi \left[ 1 + 2 \left( \frac{\sin KR_1}{KR_1} + \frac{\sin KR_2}{KR_2} \right) + \frac{\sin KR_3}{KR_3} \right] \delta(\varepsilon)$$

$$+ 2 \left[ 1 + \frac{\sin KR_1}{KR_1} - \frac{\sin KR_2}{KR_2} - \frac{\sin KR_3}{KR_3} \right] L(\Gamma_1, \varepsilon)$$

$$+ 2 \left[ 1 - \frac{\sin KR_1}{KR_1} - \frac{\sin KR_2}{KR_2} + \frac{\sin KR_3}{KR_3} \right] L(\Gamma_2, \varepsilon)$$

$$+ 2 \left[ 1 - 2 \left( \frac{\sin KR_1}{KR_1} - \frac{\sin KR_2}{KR_2} \right) - \frac{\sin KR_3}{KR_3} \right] L(\Gamma_3, \varepsilon),$$

where  $R_i = 2d \sin \left( \frac{\pi}{6} i \right)$

$$\Gamma_1 = \frac{1}{2} \frac{h}{\tau}, \quad \Gamma_2 = \frac{3}{2} \frac{h}{\tau} \quad \text{and} \quad \Gamma_3 = 2 \frac{h}{\tau}.$$

Case III: Reorientational jumps by  $30^\circ$

$$S(K, \varepsilon) = \pi A \delta(\varepsilon) + \sum_{i=1}^6 A_i L(\Gamma_i, \varepsilon),$$

where

$$A = 1 + 2 \left( \frac{\sin Kr_1}{Kr_1} + \frac{\sin Kr_2}{Kr_2} + \frac{\sin Kr_3}{Kr_3} + \frac{\sin Kr_4}{Kr_4} + \frac{\sin Kr_5}{Kr_5} \right) + \frac{\sin Kr_6}{Kr_6}$$

$$A_1 = 2 \left( 1 + \sqrt{3} \frac{\sin Kr_1}{Kr_1} + \frac{\sin Kr_2}{Kr_2} - \frac{\sin Kr_4}{Kr_4} - \sqrt{3} \frac{\sin Kr_5}{Kr_5} - \frac{\sin Kr_6}{Kr_6} \right)$$

$$A_2 = 2 \left( 1 + \frac{\sin Kr_1}{Kr_1} - \frac{\sin Kr_2}{Kr_2} - 2 \frac{\sin Kr_3}{Kr_3} - \frac{\sin Kr_4}{Kr_4} + \frac{\sin Kr_5}{Kr_5} + \frac{\sin Kr_6}{Kr_6} \right)$$

$$A_3 = 2 \left( 1 - 2 \frac{\sin Kr_1}{Kr_1} + 2 \frac{\sin Kr_4}{Kr_4} - \frac{\sin Kr_6}{Kr_6} \right)$$

$$A_4 = 2 \left( 1 - \frac{\sin Kr_1}{Kr_1} - \frac{\sin Kr_2}{Kr_2} + 2 \frac{\sin Kr_3}{Kr_3} - \frac{\sin Kr_4}{Kr_4} - \frac{\sin Kr_5}{Kr_5} + \frac{\sin Kr_6}{Kr_6} \right)$$

$$A_5 = 2 \left( 1 - \sqrt{3} \frac{\sin Kr_1}{Kr_1} + \frac{\sin Kr_2}{Kr_2} - \frac{\sin Kr_4}{Kr_4} + \sqrt{3} \frac{\sin Kr_5}{Kr_5} - \frac{\sin Kr_6}{Kr_6} \right)$$

$$A_6 = 1 - 2 \left( \frac{\sin Kr_1}{Kr_1} - \frac{\sin Kr_2}{Kr_2} + \frac{\sin Kr_3}{Kr_3} - \frac{\sin Kr_4}{Kr_4} + \frac{\sin Kr_5}{Kr_5} \right) + \frac{\sin Kr_6}{Kr_6}$$

Here

$$\Gamma_i = 2d \sin \left( \frac{\pi i}{12} \right)$$

$$\Gamma_1 = \left( 1 - \frac{\sqrt{3}}{2} \right) \frac{h}{\tau}, \quad \Gamma_2 = \frac{1}{2} \frac{h}{\tau}$$

$$\Gamma_3 = \frac{h}{\tau}$$

$$\Gamma_5 = \left(1 + \frac{\sqrt{3}}{2}\right) \frac{h}{\tau}$$

$$\Gamma_4 = \frac{3h}{2\tau}$$

$$\Gamma_6 = 2 \frac{h}{\tau}$$

In all the three cases discussed above, the scattering law consists of two parts. An elastic scattering term which is connected with long time behaviour of molecule. The second part of scattering law gives the quasielastic scattering and is controlled by the time evolution of reorientation process. The value of  $d$  is known from the structure of the molecule and the only unknown quantity in the above formulae is  $\tau$ , the time between successive reorientations.

### III. Discussions

Many molecular crystals have so-called plastic phase, which is characterised by rapid reorientational motion of the molecules. In some cases the reorientations are restricted to those about the single axis. It is known /12/ for example that electric dipole moment of t-butyl chloride (TBC),  $(\text{CH}_3)_3\text{CCl}$  molecule is frozen in space in the low temperature plastic phase of this substance. We had reported /8/ preliminary results of neutron quasielastic scattering experiments with this compound to study uniaxial reorientational motion and detailed analysis is on the way. In neutron quasielastic scattering experiments with a good resolution instrument, one expects from the above formulae a broad quasielastic spectrum centred around incident energy and a sharp elastic line sitting over this spectrum. The relative intensities of elastic and quasielastic scattering for a particular value of  $K$  is decided by the geometry of reorientations. The shape of quasielastic spectrum is decided not only by geometry but also by the rate of reorientations. In the case of quasielastic scattering

from TBC molecule, Fig.1 shows the behaviour of calculated intensity of elastic line as a function of the wave vector transfer for the three cases under consideration. The value of  $d$  was taken as  $1,81 \text{ \AA}$ . Although the three curves are similar at small  $K$ , they behave in a different fashion at large  $K$ . Thus by studying elastic intensity at various scattering angles it should be possible to decide the angular jump length. It may be pointed, however, that experimental data have to be corrected for Debye-Waller factor before comparing elastic intensities with calculated ones. It is therefore recommended to compare experimental data with theory for the ratio of elastic to quasielastic intensities at various  $K$ . Figure 2 shows the ratio of intensities of the two parts of scattering law as a function of the wave vector transfer. The information about reorientation rate is contained in quasielastic spectrum. The shape of this part of spectrum depends both on  $\tau$  and on the angular jump length  $\theta$ . When there is only one lorentzian function for  $\theta = 120^\circ$ , there are six such functions with different widths for  $\theta = 30^\circ$ . The relative intensities of these lorentzian functions also depend on  $K$ . Figure 3 shows the behaviour of these intensities as function of  $K$  for case III. Only the first and second lorentzians contribute to quasielastic spectrum at small  $K$ , but all of them become important at large  $K$ . If the value of  $\theta$  is decided by form factor measurements, the value of  $\tau$  can be obtained from the shape of quasielastic spectrum. This value should be chosen in such a way that calculated quasielastic spectra after being modified with instrument resolution compare with measured spectra at all the angles simultaneously.

The above discussions were confined to TBC molecule. But this is true in general.

Concluding we may say that neutron quasielastic scattering technique can be used to obtain information on the geometry and rate of reorientational motions of molecules in plastic solids.

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T A B L E I

Values of  $a_{ik}$  and  $b_k$  from /11/

k	1	2
$b_k$	0	3/2
$a_{ik}$ , 1	1	2
2	1	-1
3	1	-1

Case I - Reorientation jumps by 120°

k	1	2	3	4
$b_k$	0	1/2	3/2	2
$a_{ik}$ , 1	1	2	2	1
2	1	1	-1	-1
3	1	-1	-1	1
4	1	-2	2	-1
5	1	-1	-1	1
6	1	1	-1	-1

Case II - Reorientation jumps by 60°

k	1	2	3	4	5	6	7
$b_k$	0	$1-\sqrt{3}/2$	1/2	1	3/2	$1+\sqrt{3}/2$	2
$a_{ik}$ , 1	1	2	2	2	2	2	1
2	1	$\sqrt{3}$	1	0	-1	$-\sqrt{3}$	-1
3	1	1	-1	-2	-1	1	-1
4	1	0	-2	0	2	0	-1
5	1	-1	-1	2	-1	-1	-1
6	1	$-\sqrt{3}$	1	0	-1	$\sqrt{3}$	-1
7	1	$-\frac{2}{\sqrt{3}}$	2	-2	2	$\frac{2}{\sqrt{3}}$	-1
8	1	$-\sqrt{3}$	1	0	-1	$\sqrt{3}$	-1
9	1	-1	-1	2	-1	-1	-1
10	1	0	-2	0	2	0	-1
11	1	-1	-1	-2	-1	0	-1
12	1	$\sqrt{3}$	1	0	-1	$-\sqrt{3}$	-1

Case III - Reorientation jumps by 30°

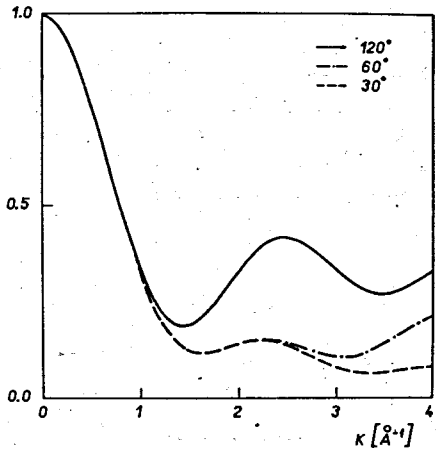


Fig.1 Form factor as a function of wave vector transfer (K).

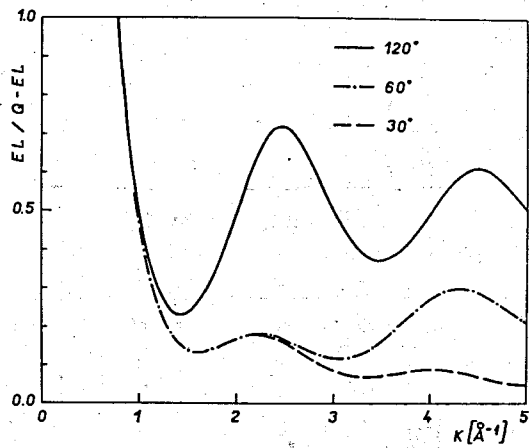


Fig.2 Ratio of elastic to quasielastic intensities as functions of wave vector transfer (K).

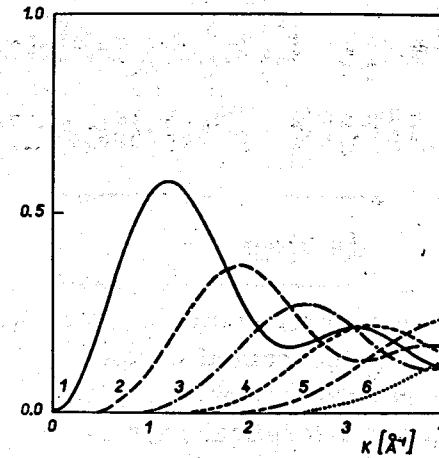


Fig.3 Relative intensities of six lorentzian functions constituting quasielastic spectrum for  $\theta = 30^\circ$  as a function of K.