Vol. A57 (1980) ACTA PHYSICA POLONICA No 5

ON STOCHASTIC JUMPS OF NH_3 MOLECULAR GROUPS IN SOLIDS

BY M. NOWOTNY-RÓŻAŃSKA

Department of Physics, Academy of Agriculture, Cracow*

AND K. ROŚCISZEWSKI

Institute of Physics, Jagellonian University, Cracow**

(Received October 22, 1979)

A model which takes crystal symmetry into account is introduced to study stochastic jumps of NH_3 groups in molecular crystals. The group theoretical method allows for the solution of this model and for finding the incoherent neutron scattering law and the infrared spectrum.

1. *Introduction*

The problem of stochastic jumps of molecular groups in molecular crystals and their influence on quasielastic incoherent neutron scattering and infrared spectrum was extensively studied in many papers [1–11]. The most frequent objects of study were NH_3, NH_4. CH_3, CH_4 groups (belonging to larger molecules). The first one — NH_3 is quite interesting and it was discussed in papers [1–3, 5, 11]. In most models it was assumed that all the stochastic jumps occur on the plane of the hydrogen triangle. The second assumption was that the reorientation was either 120 degree jumps around the three fold axis of NH_3, or that the reorientation was a simple rotational diffusion on a circle [1,5]. Neither the crystal symmetry nor its influence on NH_3 jumps was taken into account. It was thought too complicated to include in the models.

However, the application of group theory often allows for the solutions of the models with relatively high symmetry [9–11]. The example we will discuss in the present paper is the model of random jumps of the proton triangle on regular dodecagon (the twelve-fold symmetry C_{12}) which corresponds to the situation when the four fold crystal axis coincides with the three fold axis of the NH_3 group. Such a situation is quite common in cubic

---

* Address: Zakład Fizyki, Akademia Rolnicza, Mickiewicza 21, 31–120 Kraków, Poland.

** Address: Instytut Fizyki UJ, Reymonta 4, 30–059 Kraków, Poland.

molecular crystals [6]. The second and more difficult example is the model of the dodecagon with perturbed symmetry (only six fold symmetry C_6) when after a structural phase transition the four fold axis is replaced by a two fold axis in the crystal.

In the second Section of the paper we will solve these models using the methods of group theory [9–11]. In the third Section the incoherent neutron scattering law and infrared spectrum will be calculated for the models. The paper closes with a short summary.

2. *Group theoretical solutions for the system of Markov equations*

2.1. General method

To describe stochastic reorientations of the molecular group the Markov equations [12, 13] are used

$$\frac{d}{dt} P_{ij}(t) = \sum_{k} P_{ik}(t) \Lambda_{kj}, \tag{2.1}$$

where the set of numbers i, j enumerates the discrete positions of the molecular group. $P_{ij}(t)$ is the probability that the molecule orientation is the j-th one (at the time t). if at the time $t = 0$ it was the i-th. Λ_{kj} is a matrix of phenomenological constants which determine the so called relaxation times and which are parameters to be fitted from the experimental data. The diagonal matrix element Λ_{kk} (for any k) is equal to the sum of all remaining off diagonal elements from the k-th row taken with opposite signs.

The solution of the system of equation (2.1) may be easy if we assume that there exists such a matrix T that [11]

$$TPT^{\dagger} = P^{\mathrm{diag}}, \qquad TT^{\dagger} = T^{\dagger}T = 1 \tag{2.2}$$

Then also

$$T\Lambda T^{\dagger} = \Lambda^{\mathrm{diag}} \tag{2.3}$$

and

$$P_{rr}^{\mathrm{diag}}(t) = \exp\{\Lambda_{rr}^{\mathrm{diag}} \cdot t\}. \tag{2.4}$$

Applying the inverse transformation we can find the matrix P which is the solution of the system of equations (2.1).

The solution of the system of equations of the Markov type reduces to finding of the T matrix. For this purpose the symmetry of the problem must be defined.

We denote all possible orientations of a molecule by angles Ω_i where $i = 1, 2, \ldots N$. The symmetry elements g_i that form the symmetry group G of the problem transform the set Ω_i into itself: $g_i \Omega_1 = \Omega_i$.
We assume that

$$P_{ij}(t) = \int f_i^*(\Omega) \hat{\mathscr{P}}(\Omega, \Omega'|t) f_j(\Omega') d\Omega d\Omega', \tag{2.5}$$

where $\hat{\mathscr{P}}$ is an operator which does commute with all transformations of G and where f_i, f_j are basis functions which describe possible orientations of the molecule. For simplicity we take [11]

$$f_i(\Omega) = \delta(\Omega - \Omega_i). \tag{2.6}$$

Let us note that the operator of conditional probability $\hat{\mathscr{P}}$ is a two variable function defined on the group G. The functions $P_{ij}(t)$ are nothing else but a Fourier coefficients of $\hat{\mathscr{P}}$ in the basis of natural functions f_i. It is simple to show that the functions f_i form the basis of the so called regular representation of G

$$\begin{aligned} \hat{R}_{g_i} f_1(\Omega) &= f_i(\Omega), \\ \hat{R}_{g_i} f_j(\Omega) &= f_{(ij)}(\Omega), \end{aligned} \tag{2.7}$$

where $g_{ij} = g_i g_j$ and $\hat{R}_{g_i}$ denote the operator corresponding to g_i. The regular representation is reducible and according to well known theorem [14] it is possible to decompose it into the sum of all irreducible representations of G. In the system of new basis functions corresponding to irreducible representations, the matrix P will be diagonal (or quasidiagonal)

$$P_{ij}^{\text{diag}} = \langle \psi_{i(\mu i')} | \hat{\mathscr{P}} | \psi_{j(\nu j')} \rangle, \tag{2.8}$$

where $\psi_{\mu i'}$ is the i'-th basis function of the μ-th irreducible representation of G. The indices i, j give other equivalent to $(\mu i')$ enumeration of ψ.

Because $\hat{\mathscr{P}}$ commutes with all operations of G, then $P_{ij}^{\text{diag}} \neq 0$ for $i \neq j$ only when: $\mu = \nu$, $i' = j'$ and a dimension of the μ-th irreducible representation is $n_\mu > 1$.

The matrix T can be found from the formula:

$$\psi_i = \sum_j T_{ij} f_j \tag{2.9}$$

However, the matrix T from formula (2.9) is not the same as the matrix T from formula (2.2) i.e., to be more specific — using T from (2.9) we sometimes obtain P^{diag} as a quasi-diagonal matrix. Such cases can however be dealt with less difficulties.

2.2. The calculation of the matrix T for group C_{12}

Using the projection operator ϱ_n^μ we obtain the matrix T:

$$\varrho_n^\mu f_j = \frac{n_\mu}{N} \sum_{g_i} \mathscr{D}_{nn}^{\mu *}(g_i) \hat{R}_{g_i} f_j \sim \psi_{(\mu n)}, \tag{2.10}$$

where $\mathscr{D}_{nn}^{\mu}(g_i)$ is a diagonal element of the matrix of the μ-th irreducible representation corresponding to the element g_i of G. For the symmetry group $G = C_{12}$ we put into (2.10) n_μ equal to one (only one dimensional irreducible representations) and $N = 12$.

Looking at the table of characters of C_{12} we can write

$$T_{jk} = \frac{1}{\sqrt{12}} \exp\left\{\frac{2\pi i}{12}(j-1)(k-1)\right\}. \tag{2.11}$$

2.3. The model of regular dodecagon (symmetry) C_{12}

An NH_3 molecule has a three fold axis. If a crystal four fold axis coincides with it, the NH_3 molecule will be able to occupy with equal probabilities 12 different positions (hence regular dodecagon).

The probability of a jump from a position i to k in the time $dt \approx 0$ (for $i \neq j$) is [12, 13]

$$P_{ik}(dt) = A_{ik}\cdot dt. \tag{2.12}$$

We assume that the probability of a 120 degree jump (and its multiple) which does agree with the molecule three fold axis equals $a \cdot dt$. The probability of other jumps which are composed of a 90 degree jump with or without the 120 degree jump and which do change the "apparent" position of NH_3 (with respect to the crystal axis), is $b \cdot dt$. The constants a and b are phenomenological constants which one can fit from the experimental data. Then the matrix A has the following form:

$$A = \begin{bmatrix} c & b & b & b & a & b & b & b & a & b & b & b \\ b & c & b & b & b & a & b & b & b & a & b & b \\ b & b & c & b & b & b & a & b & b & b & a & b \\ b & b & b & c & b & b & b & a & b & b & b & a \\ a & b & b & b & c & b & b & b & a & b & b & b \\ b & a & b & b & b & c & b & b & b & a & b & b \\ b & b & a & b & b & b & c & b & b & b & a & b \\ b & b & b & a & b & b & b & c & b & b & b & a \\ a & b & b & b & a & b & b & b & c & b & b & b \\ b & a & b & b & b & a & b & b & b & c & b & b \\ b & b & a & b & b & b & a & b & b & b & c & b \\ b & b & b & a & b & b & b & a & b & b & b & c \end{bmatrix}, \tag{2.13}$$

where $c = -9b-2a$.

In order to simplify the calculations we write A in the form $A = cA_1+aA_2+bA_3$, where A_1, A_2, A_3 are commutting matrices composed only of numbers i.e., they are independent of any parameters and easy to diagonalise analitically.

According to the method described above we obtain:

$$P^{\text{diag}}(t) = \begin{bmatrix} 1 & & & & & & & & & & & \\ & X & & & & & & & & & & \\ & & X & & & & & & & & & \\ & & & Y & & & & & 0 & & & \\ & & & & X & & & & & & & \\ & & & & & X & & & & & & \\ & & & & & & Y & & & & & \\ & & & & & & & X & & & & \\ & & & & & & & & X & & & \\ & & & 0 & & & & & & Y & & \\ & & & & & & & & & & X & \\ & & & & & & & & & & & X \end{bmatrix} \tag{2.14}$$

where

$$A = -9b-3a, \quad B = -12b, \quad X = \exp(At), \quad Y = \exp(Bt),$$

and finally

$$P = \begin{bmatrix} k & l & l & l & m & l & l & l & m & l & l & l \\ l & k & l & l & l & m & l & l & l & m & l & l \\ l & l & k & l & l & l & m & l & l & l & m & l \\ l & l & l & k & l & l & l & m & l & l & l & m \\ m & l & l & l & k & l & l & l & m & l & l & l \\ l & m & l & l & l & k & l & l & l & m & l & l \\ l & l & m & l & l & l & k & l & l & l & m & l \\ l & l & l & m & l & l & l & k & l & l & l & m \\ m & l & l & l & m & l & l & l & k & l & l & l \\ l & m & l & l & l & m & l & l & l & k & l & l \\ l & l & m & l & l & l & m & l & l & l & k & l \\ l & l & l & m & l & l & l & m & l & l & l & k \end{bmatrix}, \tag{2.15}$$

where

$$k = \tfrac{1}{12}+\tfrac{2}{3}X+\tfrac{1}{4}Y,$$

$$m = \tfrac{1}{12}-\tfrac{1}{3}X+\tfrac{1}{4}Y,$$

$$l = \tfrac{1}{12}(1-Y).$$

All matrix multiplications were performed on a computer in Fortran.

If we assume in our model that $b = 0$ we obtain the old model of 120 degrees jumps [1, 11]:

$$P_{11}(t) = \tfrac{1}{3}(1+2e^{-3at}),$$

$$P_{15}(t) = P_{19}(t) = \tfrac{1}{3}(1-e^{-3at}). \tag{2.16}$$

2.4. The model of a dodecagon with perturbed symmetry

In this problem, exactly like in the previous model, we assume that the NH_3 molecule can occupy 12 different orientations. But now the symmetry of the problem is lower (C_6). Such a situation exists when there occurs a small distortion to the crystal (for example a structural second order phase transition) and the four fold crystal axis undergoes a transition into the two fold axis.

Positions the molecule can occupy form a regular dodecagon as before. Now, however, one set of positions (let us say, the one enumerated by odd numbers) forming the regular hexagon is distinquished from the other one. The positions of the first hexagon are the "natural" positions the NH_3 molecule can occupy i.e., they are much more probable.

The second hexagon (even numbers) is simply a set of less probable positions — we will call them the metastable ones.

We will assume that a jump from any odd position to any even one is executed with probability $c_1 dt$ (for very small time dt). The jump in the oposite direction is more probable — $c_2 \cdot dt$ where $c_1 < c_2$. Now there are the remaining probabilities (of jumps inside each hexagon) to define. The probabilities of jumps over the same angles are assumed to be the same for both hexagons. Such an assumption seems to be natural.

Like in the previous Section, the 120 degrees jump (and 240 deg one) is executed with the probability $a \cdot dt$. The probability of a jump inside one hexagon, which is composed of a 180 degree jump with or without a 120 degree jump, is assumed to be $b \cdot dt$. Now the matrix Λ has the following form:

$$\Lambda = \begin{bmatrix} \lambda_1 & c_1 & b & c_1 & a & c_1 & b & c_1 & a & c_1 & b & c_1 \\ c_2 & \lambda_2 & c_2 & b & c_2 & a & c_2 & b & c_2 & a & c_2 & b \\ b & c_1 & \lambda_1 & c_1 & b & c_1 & a & c_1 & b & c_1 & a & c_1 \\ c_2 & b & c_2 & \lambda_2 & c_2 & b & c_2 & a & c_2 & b & c_2 & a \\ a & c_1 & b & c_1 & \lambda_1 & c_1 & b & c_1 & a & c_1 & b & c_1 \\ c_2 & a & c_2 & b & c_2 & \lambda_2 & c_2 & b & c_2 & a & c_2 & b \\ b & c_1 & a & c_1 & b & c_1 & \lambda_1 & c_1 & b & c_1 & a & c_1 \\ c_2 & b & c_2 & a & c_2 & b & c_2 & \lambda_2 & c_2 & b & c_2 & a \\ a & c_1 & b & c_1 & a & c_1 & b & c_1 & \lambda_1 & c_1 & b & c_1 \\ c_2 & a & c_2 & b & c_2 & a & c_2 & b & c_2 & \lambda_2 & c_2 & b \\ b & c_1 & a & c_1 & b & c_1 & a & c_1 & b & c_1 & \lambda_1 & c_1 \\ c_2 & b & c_2 & a & c_2 & b & c_2 & a & c_2 & b & c_2 & \lambda_2 \end{bmatrix}, \tag{2.17}$$

where

$$\lambda_1 = -2a-3b-6c_1, \quad \lambda_2 = -2a-3b-6c_2.$$

2.5. The diagonalisation of the matrix Λ for the model of a perturbed dodecagon

This is a typical example when the group theory is not sufficient for the solution of (2.1). We can obtain P^{diag} in quasidiagonal form at most. This form is however such a simple form that a few "tricks" lead to the final solution with virtually no effort at all.

At first we start diagonalising Λ, using the same T matrix as for the problem with the symmetry C_{12}. Because the operator $\hat{\mathscr{P}}$ does not commute with all operations of the C_{12} group (only with those belonging also to C_6) the transformation $T\Lambda T^{\dagger}$ will not fully diagonalise the matrix Λ

$$\Lambda' = T\Lambda T^{\dagger} = \lambda_1 \Lambda'_1 + \lambda_2 \Lambda'_2 + a\Lambda'_3 + b\Lambda'_4 + c_1 \Lambda'_5 + c_2 \Lambda'_6, \tag{2.18}$$

where

$$\Lambda_1' = 0.5 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\Lambda_2' = 0.5 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$\Lambda_3' = \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$$A'_4 = \begin{bmatrix} 3&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&-3&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&3&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&-3&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0 \end{bmatrix},$$

$$A'_5 = \begin{bmatrix} 3&0&0&0&0&0&-3&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 3&0&0&0&0&0&-3&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0 \end{bmatrix},$$

$$A'_6 = \begin{bmatrix} 3&0&0&0&0&0&3&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ -3&0&0&0&0&0&-3&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0&0&0&0&0&0 \end{bmatrix}.$$

The matrices $A'_1, A'_2, \ldots A'_6$ do not commute with one another; it is difficult to diagonalise them in one single step. Therefore we will proceed in few simple steps. First we apply the transformation

$$A'' = S^{\mathrm{T}} A' S, \tag{2.19}$$

which diagonalises the matrices A_1' and A_2'. It is possible to compose S in many ways. We seek such form that A_3'', A_4'' remain diagonal and A_5'', A_6'' will become simple quasi-diagonal forms. For S we take

$$S = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \end{bmatrix} . \tag{2.20}$$

In the last step we find that the block matrix

$$\sigma = \left[\begin{array}{c|c} \sigma'_{2\times 2} & \\ \hline & \mathbf{1}_{10\times 10} \end{array}\right], \tag{2.21}$$

where

$$\sigma' = \begin{bmatrix} \frac{1}{2} & \frac{-c_1}{\sqrt{c_1^2+c_2^2}} \\ \frac{1}{2} & \frac{c_2}{\sqrt{c_1+c_2}} \end{bmatrix} \tag{2.22}$$

transforms A'' into diagonal form ($A^{\text{diag}} = \sigma^{-1}A''\sigma$):

$$A^{\text{diag}} = \begin{bmatrix} 0 & & & & & & & & & & & \\ & D & & & & & & & & & & \\ & & A & & & & & & & & & \\ & & & B & & & & 0 & & & & \\ & & & & A & & & & & & & \\ & & & & & B & & & & & & \\ & & & & & & C_1 & & & & & \\ & & & & & & & C_2 & & & & \\ & & & & & & & & A & & & \\ & & 0 & & & & & & & B & & \\ & & & & & & & & & & A & \\ & & & & & & & & & & & B \end{bmatrix}, \tag{2.23}$$

where

$$\begin{aligned}
A &= -3a - 3\mathrm{b} - 6c_1,\\
B &= -3a - 3b - 6c_2,\\
D &= -6c_1 - 6c_2,\\
C_1 &= -6c - 6c_1,\\
C_2 &= -6b - 6c_2.
\end{aligned}$$

After having finally calculated the matrix P we find that it is very complicated:

$$P = \begin{bmatrix}
k_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2\\
p_1 & k_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2\\
l_1 & p_2 & k_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & m_1 & p_2\\
p_1 & l_2 & p_1 & k_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & m_2\\
\mathrm{m}_1 & p_2 & l_1 & p_2 & k_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2\\
p_1 & m_2 & p_1 & l_2 & p_1 & k_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2\\
l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & k_1 & p_2 & l_1 & p_2 & m_1 & p_2\\
p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & k_2 & p_1 & l_2 & p_1 & m_2\\
m_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & k_1 & p_2 & l_1 & p_2\\
p_1 & m_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & k_2 & p_1 & l_2\\
l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & m_1 & p_2 & l_1 & p_2 & k_1 & p_2\\
p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & m_2 & p_1 & l_2 & p_1 & k_2
\end{bmatrix}, \tag{2.24}$$

where

$$k_1 = \frac{c_2}{6(c_1+c_2)} + \frac{c_1}{6(c_1+c_2)}\,X + \tfrac{1}{6}\,Y + \tfrac{2}{3}\,U,$$

$$k_2 = \frac{c_1}{6(c_1+c_2)} + \frac{c_2}{6(c_1+c_2)}\,X + \tfrac{1}{6}\,Z + \tfrac{2}{3}\,W,$$

$$m_1 = \frac{c_2}{6(c_1+c_2)} + \frac{c_1}{6(c_1+c_2)}\,X + \tfrac{1}{6}\,Y - \tfrac{1}{3}\,U,$$

$$m_2 = \frac{c_1}{6(c_1+c_2)} + \frac{c_2}{6(c_1+c_2)}\,X + \tfrac{1}{6}\,Z - \tfrac{1}{3}\,W,$$

$$l_1 = \frac{c_2}{6(c_1+c_2)} + \frac{c_1}{6(c_1+c_2)}\,X - \tfrac{1}{6}\,Y,$$

$$l_2 = \frac{c_1}{6(c_1+c_2)} + \frac{c_2}{6(c_1+c_2)}\,X - \tfrac{1}{6}\,Z,$$

$$p_1 = \frac{c_2}{6(c_1+c_2)}(1-X),$$

$$p_2 = \frac{c_1}{6(c_1+c_2)}(1-X).$$

We can check that for $t \to \infty$

$$P_{ik} \to \frac{c_2}{6(c_1+c_2)} \quad \text{for} \quad k = 1, 3, 5, \dots 11,$$

$$P_{ik} \to \frac{c_1}{6(c_1+c_2)} \quad \text{for} \quad k = 2, 4, 6, \dots 12. \tag{2.25}$$

This means that after a long time the system forgets the initial state from which it started at $t = 0$. Only the final state is important.

We can further consider the following limits to the model:

1) If we assume that $c_1 = c_2 = b$, then the model undergoes transition to the model of a dodecagon with C_{12} symmetry (as it should!).

2) If we assume that $c_1 = 0$, $c_2 = \infty$, we obtain the following formulas:

$$k_1 = \tfrac{1}{6}+\tfrac{1}{6}\exp(-6bt)+\tfrac{2}{3}\exp\{-(3a+3b)t\},$$

$$m_1 = \tfrac{1}{6}+\tfrac{1}{6}\exp(-6bt)-\tfrac{1}{3}\exp\{-(3a+3b)t\},$$

$$l_1 = \tfrac{1}{6}(1-\exp(-6bt)),$$

$$p_1 = \tfrac{1}{6}, \quad k_2 = m_2 = l_2 = p_2 = 0. \tag{2.26}$$

The probabilities of transitions to "metastable" states are zero. If we eliminate the metastable states then the expressions (2.26) are the same as the probabilities of transitions for the model of a regular hexagon [11].

As a closing remark let us stress that the calculation of the probability matrix P without using group theory would be very complicated. As a matter of fact we still can ask what is the use of such complicated formulas as given above. The point is, that to obtain these forms we do not have to put in any real effort. All work, all formulae can be performed *analytically* and neatly printed by a relatively little computer. The programs are simple and in Fortran. There is no need to apply high level algebraic languages like Reduce, Formac etc.

If we work without group theory and computer the effort is always incommesurable with any eventual profits.

3. The application of the models

3.1. The scattering law for quasielastic incoherent neutron scattering

The autocorrelation function, so called intermediate autocorrelation function F for quasielastic incoherent neutron scattering is well known [8]:

$$F(\boldsymbol{k}, t) = \langle \exp\{i\boldsymbol{kr}(0)\} \exp\{-i\boldsymbol{kr}(t)\}\rangle, \tag{3.1}$$

where $\hbar k$ is the transfer of the neutron momentum to the scatterer and $\boldsymbol{r}(0)$, $\boldsymbol{r}(t)$ are positions of a proton in time 0 and time t respectively. In the above formula only proton positions are taken into account because only protons contribute considerably to incoherent cross section [8].

For both models of NH_3 rotation, examined in this paper, the correlation function F for a simple molecule NH_3 has the form:

$$F(\boldsymbol{k}, t) = \sum_{i,j} P_i P_{ij}(t) \exp\{i\boldsymbol{k}(\boldsymbol{r}_i - \boldsymbol{r}_j)\}, \tag{3.2}$$

where i, j has the same meaning as in Section 2, and P_i are probabilities of finding a proton in the i-th position (at time $t = 0$).

In order to find the correlation function F_{poly} for a polycrystalline scatterer (the monocrystals are rather something exotic for an "average" experiment) we have to average over different orientations of $\boldsymbol{k}$, because the NH_3 molecules in polycrystalline sample take all possible orientations with respect to a fixed vector $\boldsymbol{k}$. Knowing F_{poly} we can find the scattering law for quasielastic incoherent neutron scattering

$$\begin{aligned} S_{\text{inc}}^{\text{poly}}(k, \omega) &= \frac{1}{2\pi} \int\limits_{-\infty}^{+\infty} \exp(-i\omega t) \cdot dt \cdot F(k, t)_{\text{poly}} \\ &= \tfrac{1}{12}\left\{\delta(\omega)\left[1 + \frac{2\sin(kR_1)}{kR_1} + \frac{2\sin(kR_2)}{kR_2} + \frac{2\sin(kR_3)}{kR_3}\right.\right. \\ &\qquad \left. + \frac{2\sin(kR_4)}{kR_4} + \frac{2\sin(kR_5)}{kR_5} + \frac{\sin(kR_6)}{kR_6}\right] \\ &\qquad + \frac{8}{\pi}\left(1 - \frac{\sin(kR_4)}{kR_4}\right)\frac{\Gamma_1}{\Gamma_1^2+\omega^2} + \frac{3}{\pi}\left(1 + \frac{2\sin(kR_4)}{kR_4}\right. \\ &\qquad - \tfrac{2}{3}\frac{\sin(kR_1)}{kR_1} - \tfrac{2}{3}\frac{\sin(kR_2)}{kR_2} - \tfrac{2}{3}\frac{\sin(kR_3)}{kR_3} - \tfrac{2}{3}\frac{\sin(kR_5)}{kR_5} \\ &\qquad \left.\left. - \tfrac{1}{3}\frac{\sin(kR_6)}{kR_6}\right)\frac{\Gamma_2}{\Gamma_2^2+\omega^2}\right\} = F_0 \cdot \delta(\omega) + F_1 \frac{\Gamma_1}{\Gamma_1^2+\omega^2} + F_2 \frac{\Gamma_2}{\Gamma_2^2+\omega^2}, \end{aligned} \tag{3.3}$$

where $\Gamma_1 = 9b+3a$, $\Gamma_2 = 12b$, $R_n = 2d \sin\frac{n\pi}{12}$ for $n = 1, 2, 3, 4, 5$, and where d is the distance from the centre of a proton triangle to any proton.

As we see the Van Hove function $S_{\text{inc}}^{\text{poly}}$ for the model of the dodecagon with C_{12} symmetry is composed of an elastic peak and two lorentzians with half widths $\Gamma_1 = 3a+9b$, $\Gamma_2 = 12b$. The corresponding form factors are presented in Fig. 1.

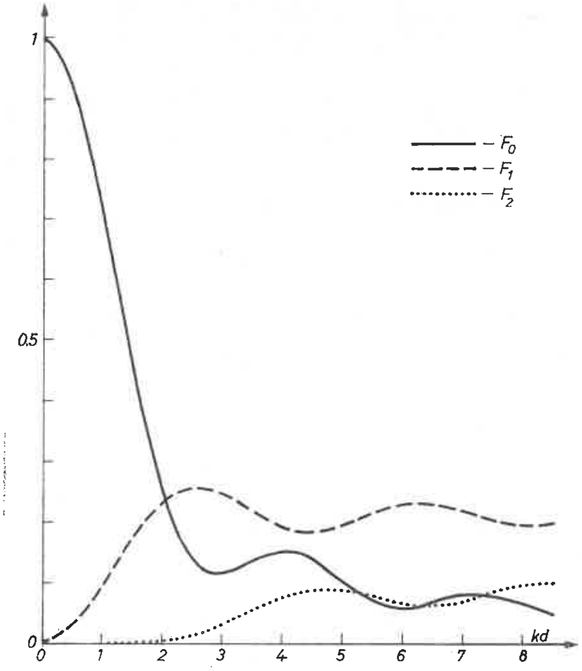

Fig. 1. The dependence of the elastic formfactor F_0 and formfactors F_1, F_2 on dimensionless value of (kd)

The scattering law for the model of the dodecagon with perturbed symmetry is

$$
\begin{aligned}
S_{\mathrm{inc}}(k,\omega) = \frac{1}{6(c_1+c_2)}\Bigg\{ & \delta(\omega)\left[\frac{c_1^2+c_2^2}{c_1+c_2}\left(1+2f\left(\frac{\pi}{3}\right)+2f\left(\frac{\pi}{6}\right)+f\left(\frac{\pi}{2}\right)\right)\right. \\
& \left. +\frac{2c_1c_2}{c_1+c_2}\mathscr{A}\right]+\frac{\Gamma_1}{\Gamma_1^2+\omega^2}\left[\frac{2c_1c_2}{\pi(c_1+c_2)}\left(1+2f\left(\frac{\pi}{3}\right)+2f\left(\frac{\pi}{6}\right)+f\left(\frac{\pi}{2}\right)-\mathscr{A}\right)\right] \\
& +\frac{\Gamma_2}{\Gamma_2^2+\omega^2}\left[\frac{c_2}{\pi}\left(1+2f\left(\frac{\pi}{3}\right)-2f\left(\frac{\pi}{6}\right)-f\left(\frac{\pi}{2}\right)\right)\right] \\
& +\frac{\Gamma_3}{\Gamma_3^2+\omega^2}\left[\frac{c_1}{\pi}\left(1+2f\left(\frac{\pi}{3}\right)-2f\left(\frac{\pi}{6}\right)-f\left(\frac{\pi}{2}\right)\right)\right] \\
& +\frac{\Gamma_4}{\Gamma_4^2+\omega^2}\left[\frac{4c_2}{\pi}\left(1-f\left(\frac{\pi}{3}\right)\right)\right]+\frac{\Gamma_5}{\Gamma_5^2+\omega^2}\left[\frac{4c_1}{\pi}\left(1-f\left(\frac{\pi}{3}\right)\right)\right]\Bigg\}, \qquad (3.4)
\end{aligned}
$$

where

$$\Gamma_1 = 6(c_1+c_2), \quad \Gamma_2 = 6(b+c_1), \quad \Gamma_3 = 6(b+c_2), \quad \Gamma_4 = 3a+3b+6c_1,$$

$$\Gamma_5 = 3a+3b+6c_2,$$

$$f(\beta) = \frac{\sin(2kd\sin\beta)}{2kd\sin\beta},$$

$$\underset{\alpha=2\pi/12}{\mathscr{A}} = f\left(\frac{\alpha}{2}\right) + f\left(\frac{\pi}{6} - \frac{\alpha}{2}\right) + f\left(\frac{\pi}{6} + \frac{\alpha}{2}\right) + f\left(\frac{\pi}{3} - \frac{\alpha}{2}\right) + f\left(\frac{\pi}{3} + \frac{\alpha}{2}\right) + f\left(\frac{\pi}{2} - \frac{\alpha}{2}\right).$$

There is an elastic peak and five lorentzians with half widths Γ_1, Γ_2, Γ_3, Γ_4, Γ_5.

3.2. The correlation functions and the shape of the infrared spectrum

The correlation function for IR spectrum is given by [7]

$$F(t) = \langle \boldsymbol{\mu}(0)\boldsymbol{\mu}(t)\rangle. \tag{3.5}$$

where $\boldsymbol{\mu}(0)$, $\boldsymbol{\mu}(t)$ denote the dipole moment of a vibrational transition of a molecule at times 0 and t, respectively. The change in time of $\boldsymbol{\mu}$ is due to a composition of two processes: pure vibration of the molecule and pure rotational reorientation. To make the dependence of F on these two processes explicit, we will proceed as follows. Let us decompose the dipole moment into "spherical" components:

$$\boldsymbol{\mu} = (\mu_1, \mu_{-1}, \mu_0), \tag{3.6}$$

where

$$\mu_1 = \frac{1}{\sqrt{2}}(\mu_x + i\mu_y), \qquad \mu_{-1} = -\mu_1^*, \qquad \mu_0 = \mu_z,$$

and

$$\boldsymbol{\mu}(0)\boldsymbol{\mu}(t) = \sum_{m=-1}^{1} \mu_m^*(0)\mu_m(t).$$

The molecules in a polycrystalline sample are differently oriented in space. We assume that a certain molecule has at $t = 0$ an orientation defined by Euler angles $\alpha(0)$, $\beta(0)$, $\gamma(0)$. We further assume (without loss of generality) that in the coordinate system fixed in the molecule the dipole moment is $\boldsymbol{\mu}^0$ and that $\mu_y^0 = \mu_z^0 = 0$, $\mu_x^0 \neq 0$.

Applying Wigner rotation matrices D we obtain:

$$\mu_m(t) = \sum_r D^1_{mr}(\alpha(t), \beta(t), \gamma(t))\mu_r^0(t). \tag{3.7}$$

Inserting (3.7) into (3.5) we obtain the formula for the polycrystalline correlation function:

$$F(t)_{\text{poly}} = \sum_{m,n,r} \langle D^{1*}_{m,n}(\alpha(0), \beta(0), \gamma(0)) D^1_{mr}(\alpha(t), \beta(t), \gamma(t)) \mu_n^{*0}(0)\mu_r^0(t)\rangle|_{\alpha(0),\beta(0),\gamma(0)}\,. \tag{3.8}$$

where there is an additional average over $\alpha(0)$, $\beta(0)$, $\gamma(0)$.

The common approximation to (3.8) is

$$F(t)_{\text{poly}} \cong \sum_{m,n,r} \langle D^{1*}_{mn}(\ldots) D^1_{mr}(\ldots)\rangle \langle \mu_n^{0*}(0)\mu_r^0(t)\rangle, \tag{3.9}$$

where $\langle \mu_n^{0*}(0)\mu_r^0(t)\rangle$ is simply $\langle \mu_x^{0*}(0)\mu_x^0(t)\rangle$ multiplied by 1/2 for $n = r = \pm 1$, or by $-1/2$ for $n = -r = \pm 1$, or it is zero. The expression $\langle \mu_x^{*0}(0)\mu_x^0(t)\rangle$ is a pure vibrational correlation function —$f_{\mathrm{vibr}}(t)$ (because is independent of the reorientation of the molecule).

Both models of NH_3 rotational reorientation used in this paper are planar. Therefore it results that:

$$\alpha(0) = \alpha(t) = \alpha, \qquad \beta(0) = \beta(t) = \beta,$$
$$\gamma(0) = \gamma, \qquad \gamma(t) = \gamma + \varphi(t). \tag{3.10}$$

Using the well known properties of D matrices we obtain:

$$F_{\mathrm{poly}}(t) = \sum_{m=\pm 1,0} \frac{1}{8\pi^2} \iiint \{\langle D_{mn}^{1*}(\alpha\beta\gamma) D_{mn}^{1}(\alpha\beta\gamma) e^{in\varphi(t)}\rangle$$
$$-\langle D_{mn}^{*1}(\alpha\beta\gamma) D_{m,-n}^{1}(\alpha\beta\gamma) e^{in\varphi(t)}\rangle\} \tfrac{1}{2} f_{\mathrm{vibr}}(t) d\alpha d\beta d\gamma \sin\beta = f_{\mathrm{vibr}}(t)\langle\cos\varphi(t)\rangle$$
$$= f_{\mathrm{vibr}}(t) f_{\mathrm{rot}}(t). \tag{3.11}$$

The formula for f_{rot} is

$$f_{\mathrm{rot}}(t) = \langle\cos\varphi(t)\rangle = \sum_{i,j} P_i P_{ij}(t)\cos\varphi_{ij}, \tag{3.12}$$

where φ_{ij} is an angle over which the molecule jumps from the i-th to the j-th position (in time t).

For the model of a regular dodecagon for which $P_i = 1/12$ (for all i) we obtain

$$f_{\mathrm{rot}}(t) = \exp\{-(9b+3a)t\}. \tag{3.13}$$

The Fourier transform of f_{rot} gives the broadening of the vibrational peak and the shape of the infrared spectrum is proportional to

$$\left\{\int e^{-i\omega t}\cdot dt \cdot f_{\mathrm{vibr}}(t)\right\} \cdot \frac{\Gamma_1}{\Gamma_1^2+\omega^2}, \tag{3.14}$$

where $\Gamma_1 = 3a+9b$

For the model of a dodecagon with perturbed symmetry the time dependent correlation function and its Fourier transform are

$$f_{\mathrm{rot}}(t) = \frac{c_2}{c_1+c_2}\exp\{-(3a+3b+6c_1)t\} + \frac{c_1}{c_1+c_2}\exp\{-(3a+3b+6c_2)t\}; \tag{3.15}$$

$$\int f_{\mathrm{rot}}(t)\exp(-i\omega t)\cdot dt = \frac{c_2}{\pi(c_1+c_2)}\frac{\Gamma_4}{\Gamma_4^2+\omega^2} + \frac{c_1}{\pi(c_1+c_2)}\frac{\Gamma_5}{\Gamma_5^2+\omega^2}, \tag{3.16}$$

where $\Gamma_4 = 3a+3b+6c_1$, $\Gamma_5 = 3a+3b+6c_2$.

Let us stress that the $\Gamma_1, \Gamma_2, \ldots \Gamma_5$ given above are exactly the same as the corresponding $\Gamma_1, \Gamma_2, \ldots \Gamma_5$ for neutrons.

4. Conclusions

In this paper two models of planar rotation of the NH_3 group in solids are considered. One is the model of a regular dodecagon and the other is a dodecagon with perturbed symmetry. These models describe jumps of NH_3 groups when the three fold axis of NH_3 coincides with the four fold (or two fold) axis of the crystal.

The models are solved analytically by the methods of group theory and the rotational correlation functions are found for quasielastic incoherent neutron scattering and for the infrared spectrum.

The results of the paper can be directly applied to the analysis of experimental data. They can give a more precise description of molecular reorientations in some experiments (see for example [1, 6]) provided the simpler models used up to now were found unsatisfactory. What is more, the present models combined together can serve to fit the experimental data at different temperatures of the crystal even in the case of phase transition which makes the use of one model on both sides of transition temperature a little suspicious.

The authors would like to thank Professor J. Janik and Professor A. Fuliński for stimulating this work and for encouragement. Thanks are also due to dr K. Sokalski for his valuable comments and discussions on the group theoretical method used in this paper.

REFERENCES

[1] J. A. Janik, J. M. Janik, K. Otnes, K. Rościszewski, *Physica* **83B**, 259 (1976).

[2] K. Skold, U. Dahlborg, *Solid State Commun.* **13**, 543 (1973).

[3] H. J. Prask, S. F. Trevino, J. J. Rush, *J. Chem. Phys.* **62**, 4156 (1975).

[4] K. Skold, *J. Chem. Phys.* **49**, 2443 (1968).

[5] P. S. Goyal, N. Nawrocik, S. Urban, J. Domosławski, I. Natkaniec, *Acta Phys. Pol.* **A46**, 399 (1974).

[6] J. M. Janik, A. Migdał-Mikuli, J. A. Janik, *Acta Phys. Pol.* **A46**, 299 (1974).

[7] R. G. Gordon, *J. Chem. Phys.* **43**, 1307 (1965).

[8] P. A. Egelstaff, *J. Chem. Phys.* **53**, 2590 (1970).

[9] A. J. Dianoux, F. Volino, H. Hervet, *Mol. Phys.* **30**, 1181 (1975).

[10] G. Williams, M. Cook, *J. Chem. Soc. Faraday Trans.* **67**, 990 (1971).

[11] K. Rościszewski, *On the problem of stochastic jumps of molecules in solids. Group theory analysis.* Preprint SSPUJ-14/77, Cracow 1977.

[12] A. T. Bharucha-Reid, *Elements of the theory of Markov processes and their applications*, McGraw–Hill, New York 1960.

[13] W. Feller, *An introduction to probability theory and its applications*, PWN, Warsaw 1960.

[14] M. Hammermesh, *Group theory and its application to physical problems* Addison–Wesley, Mass. 1962.