WOLFF, P. M. DE (1974). *Acta Cryst.* A30, 777–785.
WOLFF, P. M. DE (1977). *Acta Cryst.* A33, 493–497.
WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A37, 625–636.
YAMAMOTO, A. (1982). *Acta Cryst.* A38, 87–92.

YAMAMOTO, A., JANSSEN, T., JANNER, A. & DE WOLFF, P. M. (1985). *Acta Cryst.* A41, 528–530.
YAMAMOTO, N. (1988). *Solid State Phys.* 23, 547–556.
YAMAMOTO, N., HIROTSU, Y., NAKAMURA, Y. & NAGAKURA, S. (1989). *Jpn. J. Appl. Phys.* 28, L598–L601.

2D Rotation–Translation Coupling with Planar Molecules

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Abstract

A structure-factor calculation for 2D rotation–translation coupling with planar molecules is presented. The starting point is a continuous description of the scattering-length-density distribution for a planar molecule that rotates around its symmetry axis. For the example of a molecule with threefold symmetry at a site with fourfold symmetry, the successive correction terms to the conventional rotational form factor are evaluated. This approach yields results equivalent to the split-molecule model. This is shown by an example of a structure refinement on $Ni(ND_3)_6Br_2$ single-crystal data.

1. Introduction

The description of the thermal motion in the structure analysis of more complex molecular solids continues to be a difficult problem. Particularly in the presence of orientational disorder, powder samples give rise to only a few Bragg peaks of notable intensity, while there may be many model parameters. For atoms (ions), a rather detailed description of the probability density functions (p.d.f.) beyond harmonic motions or the corresponding structure factors are available [cumulant expansion, Gram-Charlier expansion (*International Tables for X-ray Crystallography*, 1974)]. Frequently, disorder aspects are described by split-atom models. For (rigid) molecules or molecular groups, the above approaches can be used for describing the centre-of-mass (c.o.m.) positions of the molecules. Additionally, rotational motions and, possibly, orientational disorder have to be introduced. Again this can be done either with continuous or with discrete models. In the first case, the density distribution on a spherical surface (2D: circle) is expanded into symmetry-adapted surface harmonics (2D: trigonometric functions). In the second case, an appropriate set of discrete molecular orientations is chosen.

Apparently, there are cases where c.o.m. motions and rotational motions do not occur independently and there is a pronounced rotation–translation coupling (RT coupling). A three-dimensional example, CBr_4-I, was described quite a while ago (Press, Grimm & Hüller, 1979; Hohlwein, 1984).

(i) In the first case, a p.d.f., containing both a positional (c.o.m.) and an angular variable, is expanded (Taylor expansion) into symmetry-allowed terms and powers of displacement variables and derivatives of the p.d.f. are combined to give products that are totally symmetric with respect to the symmetry operations of the site symmetry. One may note a simple meaning of RT coupling: the orientational distribution depends on the c.o.m. position, which means that it is different for the equilibrium or displaced c.o.m. position. This is most pronounced for asymmetric molecules (like triangular groups *etc.*) at a site with a centre of symmetry.

(ii) An equivalent access is the 'split-molecule' approach, which can be introduced in two successive steps. C.o.m. displacements lead to low-symmetry sites with a preference for certain orientations. The first approach consists in taking a discrete distribution of the c.o.m.'s over all symmetrically equivalent sites of a lattice position in combination with continuous orientational distributions. It is not particularly useful for practical purposes, but demonstrates the meaning of the model parameters of (i) more explicitly. The most general split-molecule approach uses one or several discrete c.o.m. positions and a set of discrete orientations. A p.d.f. conforming with the

site symmetry is guaranteed by applying the appropriate symmetry operations and has all the advantages and disadvantages of an unspecific model.

A first paper (Press, Grimm & Hüller, 1979) dealt with 3D rotating molecules in the continuous description. The transition to the simpler case of a single rotational degree of freedom is nontrivial and appears useful. Also, there is recent evidence for the importance of RT coupling for ND_3 motion in $Ni(ND_3)_6Br_2$ and related compounds (Hoser, Prandl, Schiebel & Heger, 1990; Schiebel, Hoser, Prandl & Heger, 1990). However, as will be seen in the study of specific examples, the neglect of the 3D aspect of motions is not always obvious.

In §2, we discuss the rotation–translation coupling for planar molecules with a single rotational degree of freedom in a continuous description analogous to that given by Press, Grimm & Hüller (1979). The third chapter deals with the split-molecule approaches. Finally, several models are discussed using recent neutron data for $Ni(ND_3)_6Br_2$.

2. Inclusion of rotation–translation coupling for a planar (triangular) molecule

In a previous paper (Press, Grimm & Hüller, 1979), we have given a formulation only for the correlations between orientation and c.o.m. position of 3D molecular rotation, with CH_4 and CN groups as examples. Below we derive the corresponding expressions for a 1D rotor (planar molecules such as CH_3 groups, NH_3NO_3 etc.). The calculation is performed along the same lines as in Press, Grimm & Hüller (1979), while the starting point is that of Press & Hüller (1973).

According to Press & Hüller (1973), the density distribution $\rho(\mathbf{r})$ can be expressed in terms of a translational p.d.f. and a conditional probability $\rho_{rot}(\mathbf{r}'|\mathbf{R})$ of finding a scatterer at $\mathbf{r}' = \mathbf{r} - \mathbf{R}$ if the molecular centre of mass is at $\mathbf{R}$:

$$\rho(\mathbf{r}) = \int \rho_T(\mathbf{R})\rho_{rot}(\mathbf{r}'|\mathbf{R})\, d\mathbf{R}. \tag{1}$$

In ρ_{rot}, the orientational distribution depends on the centre-of-mass position, that is, the effect of steric hindrance on asymmetric molecules may be included. ρ_T is the translational p.d.f. of the molecular c.o.m. As has been suggested previously (Press, Grimm & Hüller, 1979), $\rho_{rot}(\mathbf{r}'|\mathbf{R})$ is then expanded into a Taylor series. This is permissible as long as the translational displacements $\mathbf{R}' = \mathbf{R} - \mathbf{R}_0$ are small* ($\mathbf{R}_0 =$ mean c.o.m. position):

$$\rho_{rot}(\mathbf{r}'|\mathbf{R}) = \rho_{rot}^{(0)}(\mathbf{r}') + \rho_{rot}^{(1)}(\mathbf{r}')\mathbf{R}' + \tfrac{1}{2}\mathbf{R}'\rho_{rot}^{(2)}(\mathbf{r}')\mathbf{R}' + \dots, \tag{2}$$

with $\rho_{rot}^{(0)}(\mathbf{r}') = \rho_{rot}(\mathbf{r}'|\mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}$ the well known orientational p.d.f., which reflects both the molecular and the

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* As the values of $\mathbf{R}'$ are small compared to $\mathbf{R}_0$ and $\mathbf{r}'$, the notation $\Delta\mathbf{R}'$ would be preferable but we continue the notation of Press & Hüller (1973).

site symmetry. $\rho_{rot}^{(1)}(\mathbf{r}')$ is a vector with two components, $\alpha = x, y$:

$$[\rho_{rot}^{(1)}(\mathbf{r}')]_\alpha = \frac{\partial}{\partial R_\alpha}\rho_{rot}(\mathbf{r}'|\mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}$$

and $\rho_{rot}^{(2)}(\mathbf{r}')$ is a 2×2 tensor with elements

$$[\rho_{rot}^{(2)}(\mathbf{r}')]_{\alpha\beta} = \frac{\partial}{\partial R_\alpha}\frac{\partial}{\partial R_\beta}\rho_{rot}(\mathbf{r}'|\mathbf{R})|_{\mathbf{R}=\mathbf{R}_0}.$$

The structure factor, correspondingly, may be written as

$$F_{rot}(\mathbf{Q}) = \sum_l F_{rot}^{(l)}(\mathbf{Q}), \tag{3}$$

where the different orders l correspond to the order of the expansion in (2).

As $\rho_T(\mathbf{R})$ has the full site symmetry (or even higher symmetry, in the case of an isotropic Debye–Waller factor), $\rho_{rot}(\mathbf{r}'|\mathbf{R})$ must possess full site symmetry, too. The example that we shall discuss is that of a triangular group (symmetry $3m$) at a site with symmetry $4mm$, which is realized by an ND_3 group with symmetry axis along cubic axes, as in $Ni(ND_3)_6Br_2$.

2.1. Conventional rotational form factor

For a planar molecule that rotates around its (primary) symmetry axis, the probability density $\rho_{rot}^{(0)}(\mathbf{r}')$, or the corresponding scattering-length density, can be written as

$$\rho_{rot}^{(0)}(\mathbf{r}') = (1/2\pi r)\delta(r' - \varrho)\delta(z')g(\varphi_r').$$

Here, cylindrical coordinates $\mathbf{r}' = (r', \varphi_r', z')$ have been used; ϱ is the distance of the atoms from the molecular centre of mass. $g(\varphi_r')$ is expanded into trigonometric functions and

$$g(\varphi') = \sum_{m=0}^{\infty}[c_m \exp(im\varphi_r') + c_{-m}\exp(-im\varphi_r')].$$

If $g(\varphi_r') = g(-\varphi_r')$, that is in the presence of a mirror plane, c_m is real and $c_m = c_{-m}$. As in Press & Hüller (1973) a 'formal development' can be made that is based on an expansion of the density distribution in a molecular frame (this introduces the molecular symmetry), a transformation $\Delta\varphi$ to the crystal frame (this introduces the site symmetry) and a distribution function $f(\Delta\varphi)$ for this angle $\Delta\varphi$ (see Appendix). The structure factor, taken in units of the scattering length of the rotating atoms ($3b_D$ for ND_3),

$$F_{rot}^{(0)}(\mathbf{Q}) = \int \rho_{rot}^{(0)}(\mathbf{r}')\exp(i\mathbf{Q}\mathbf{r}')\, d\mathbf{r}',$$

is calculated after expansion of the second factor in

$$\exp(i\mathbf{Q}\mathbf{r}') = \exp(iQ_z z')\exp[iQ_r r'\cos(\varphi_Q - \varphi_r')]$$

with $\mathbf{Q} = (Q_r, \varphi_Q, Q_z)$ into Bessel functions (J_l). After integration over $\mathbf{r}'$, the structure factor is obtained.

$$F_{\text{rot}}^{(0)}(\mathbf{Q}) = \sum_{l=0}^{\infty} i^l J_l(Q_r\varrho)\{c_l \exp(il\varphi_Q) + c_{-l}\exp(-il\varphi_Q)\}.$$

If the density distribution in real space is expressed in terms of $\cos(3m\varphi_r')$ and $\sin(3m\varphi_r')$, exactly these expressions with $\varphi_r' \to \varphi_Q$ reappear in the curly brackets. If we return to our specific example of a triangular molecule (equilateral triangle) with a fourfold cubic axis as normal, only indices $m = 4m'$ and hence arguments $12m'\varphi_r'$ are allowed. As in Press & Hüller (1973), all terms in (3) should be multiplied by $\exp(i\mathbf{Q}\mathbf{R_0})\exp[-W(\mathbf{Q})]$, thus introducing the centre-of-mass position of the planar groups and a Debye–Waller factor, which is isotropic within the $Q_x - Q_y$ plane. This description of the structure factor can easily be generalized to several molecular groups.

An anisotropy of the Debye–Waller factor or higher cumulants of a displaced molecule certainly may be introduced. But this renders the calculation somewhat more tedious.

2.2. $F_{\text{rot}}^{(1)}(\mathbf{Q})$: linear coupling

As for the case of a 3D rotator, the product $\rho_{\text{rot}}^{(1)}(\mathbf{r'})\mathbf{R'}$ must have the full site symmetry, i.e. belong to the identity representation which is $\Gamma = A_1$, for the point group $4mm$. $[\rho_{\text{rot}}^{(1)}(\mathbf{r'})]_\alpha$ and R'_α, therefore, must belong to the same representations $\tilde{\Gamma}$ (Lax, 1974) and, as $\mathbf{R'}$ is involved, this is the vector representation. The displacement vector $\mathbf{R'} = |\mathbf{R'}|(\cos\varphi_R', \sin\varphi_R')$ has E symmetry, so only terms with E symmetry are retained in the Fourier series of $[\rho_{\text{rot}}^{(1)}(\mathbf{r'})]$. In $4mm$, these are pairs of functions $\cos l\varphi_r'$, $\sin l\varphi_r'$ with l odd so

$$\rho_{\text{rot}}^{(1)}(\mathbf{r'}) = \frac{1}{2\pi r'}\delta(r' - \varrho)\delta(z')\sum_{l\in\tilde{\Gamma}=E} c_l^{(1)}(\cos l\varphi_r', \pm\sin l\varphi_r')$$

combine to totally symmetric invariants in the structure factor. With $F_{\text{rot}}^{(1)}(\mathbf{Q})$ again taken in units of the scattering length of the rotating atoms,

$$F_{\text{rot}}^{(1)}(\mathbf{Q}) = \sum_{l=0}^{\infty} i^l J_l(Q_r\varrho)i\langle u^2\rangle$$
$$\times Q_r c_l^{(1)}(\cos\varphi_Q\cos l\varphi_Q \pm \sin\varphi_Q\sin l\varphi_Q).$$

Because of the molecular symmetry, only trigonometric functions of order $l = 3\tilde{l}$, $\tilde{l}$ odd contribute. Group theoretical considerations give the sign in the bracket: $-$ for $l = 3$, $+$ for $l = 9$, $-$ for $l = 15$ etc.

Explicitly, for equilateral-triangle-type molecules, the two leading terms read

$$F_{\text{rot}}^{(1)}(\mathbf{Q}) = \langle u^2\rangle Q_r\{J_3(Q_r\varrho)c_3^{(1)}(\cos\varphi_Q\cos 3\varphi_Q$$
$$- \sin\varphi_Q\sin 3\varphi_Q)$$
$$-J_9(Q_r\varrho)c_9^{(1)}(\cos\varphi_Q\cos 9\varphi_Q$$
$$+ \sin\varphi_Q\sin 9\varphi_Q) \pm \ldots\}$$

$$= \langle u^2\rangle Q_r J_3(Q_r\varrho)c_3^{(1)}\cos 4\varphi_Q$$
$$-\langle u^2\rangle Q_r J_9(Q_r\varrho)c_9^{(1)}\cos 8\varphi_Q + \ldots.$$

$F_{\text{rot}}^{(1)}(\mathbf{Q})$ is the leading correction term to the usual rotational form factor $F_{\text{rot}}^{(0)}(\mathbf{Q}) = F_{\text{rot}}(\mathbf{Q})$. There are rather few trigonometric functions contributing, as only terms which fulfil the conditions of molecular symmetry and transform like a vector are nonzero. Additionally, the Bessel functions $J_l(Q_r\varrho)$ ensure rapid convergence if the argument $Q_r\varrho$ is not too large. The $c_l^{(1)}$ have the dimension of reciprocal length. The appropriate quantity for further discussion is the product $c_l^{(1)}\langle u^2\rangle$: it is large when both c.o.m. displacement *and* departures from the average symmetry accompanying these displacements (due to steric hindrance effects, for example) become large. We shall return to this in the next section.

2.3. $F_{\text{rot}}^{(2)}(\mathbf{Q})$: quadratic coupling

Next we give the results for a quadratic coupling, which is also present for molecules with a centre of symmetry. $x^2 - y^2 = R'^2\cos 2\varphi_R'$ and $2xy = R'^2\sin 2\varphi_R'$ have B_1 and B_2 symmetry, respectively. As before, only trigonometric functions that have the same symmetry B_1, B_2 contribute as the sums of the product $\mathbf{R'}\rho_{\text{rot}}^{(2)}(\mathbf{r'})\mathbf{R'}$ must be totally symmetric. Therefore, only terms of order $l = 6$ have to be included in our example of an equilateral triangle at a site of symmetry $4mm$ (higher-order terms $l = 18, 30, \ldots$ can be neglected).

$$\mathbf{R'}\rho_{\text{rot}}^{(2)}(\mathbf{r'})\mathbf{R'} = \sum_{\alpha,\beta} [R'_\alpha(\varphi_R'), R'_\beta(\varphi_R')]$$
$$\times \begin{pmatrix} [\rho_{\text{rot}}^{(2)}(r')]_{\alpha\alpha} & [\rho_{\text{rot}}^{(2)}(r')]_{\alpha\beta} \\ [\rho_{\text{rot}}^{(2)}(r')]_{\beta\alpha} & [\rho_{\text{rot}}^{(2)}(r')]_{\beta\beta} \end{pmatrix}$$
$$\times \begin{pmatrix} R'_\alpha(\varphi_R') \\ R'_\beta(\varphi_R') \end{pmatrix}$$
$$= \frac{1}{2\pi r'}\delta(r' - \varrho)\delta(z')\{c_{6,B_1}^{(2)}\cos 6\varphi_r'$$
$$+ c_{6,B_2}^{(2)}\sin 6\varphi_r' + \ldots\} \quad (4)$$

$$F_{\text{rot}}^{(2)}(\mathbf{Q}) = \langle u^2\rangle^2 Q_r^2 J_6(Q_r\varrho)$$
$$\times \left\{\frac{c_{6,B_1}^{(2)} + c_{6,B_2}^{(2)}}{2}\cos(4\varphi_Q)\right.$$
$$\left. + \frac{c_{6,B_1}^{(2)} - c_{6,B_2}^{(2)}}{2}\cos(8\varphi_Q)\right\} + \ldots. \quad (5)$$

For large-amplitude centre-of-mass motions, $F_{\text{rot}}^{(2)}(\mathbf{Q})$ may well be a sizable contribution to the structure factor. Note that the magnitude of the contribution is now $\sim \langle u^2\rangle^2$.

3. 'Split-molecule' approach

As an alternative, a generalized version of Guthrie & McCullough's (1961) method, also called the Frenkel model,

Table 1. *Comparison of the different models for the* $Ni(ND_3)_6Br_2$ *data*

Model		A	B	C	D	E
Scale		17.3 (4)	17.4 (2)	17.4 (2)	17.3 (2)	17.6 (1)
X (D3)	(Å)				−0.126 (5)	−0.145 (6)
Y (D3)	(Å)				0.102 (1)	0.127 (4)
Z (D3)	(Å)	2.505 (6)	2.510 (2)	2.510 (2)	2.509 (3)	2.506 (3)
φ (D3)	(°)				4 (1)	48.7
θ (D3)	(°)					−6.5 (4)
ψ (D3)	(°)					−20 (1)
$c_3^{(1)}$	(Å⁻¹)		−2.50 (9)	−2.50 (9)		
$c_9^{(1)}$	(Å⁻¹)			0.3 (9)		
$c_{6,B_1}^{(2)}$	(Å⁻²)			1.1 (7)		
$c_{6,B_2}^{(2)}$	(Å⁻²)			−2.3 (7)		
ϱ (D3)	(Å)	0.92 (1)	0.944 (4)	0.946 (4)	0.948 (4)	0.953 (2)
h (ND3)	(Å)	0.36 (1)	0.362 (4)	0.362 (4)	0.361 (4)	0.361 (3)
$\langle u^2 \rangle_{Ni}$	(Å²)	0.021 (2)	0.0222 (8)	0.0220 (7)	0.0219 (7)	0.0219 (4)
$\langle u^2 \rangle_{Br}$	(Å²)	0.032 (2)	0.033 (1)	0.034 (1)	0.034 (1)	0.0342 (6)
$\langle u^2 \rangle_{N_\parallel}$	(Å²)	0.042 (2)	0.0411 (8)	0.0414 (7)	0.0288 (9)	0.0287 (5)
$\langle u^2 \rangle_{N_\perp}$	(Å²)	0.028 (3)	0.028 (1)	0.028 (1)	0.025 (4)	0.032 (2)
$\langle u^2 \rangle_{D_\parallel}$	(Å²)	0.052 (4)	0.058 (2)	0.058 (2)	0.049 (1)	0.0450 (8)
$\langle u^2 \rangle_{D_\perp}$	(Å²)	0.054 (4)	0.049 (2)	0.049 (2)	0.048 (2)	0.036 (3)
Parameters		10	11	14	13	14
R		0.16	0.081	0.075	0.076	0.053
R_w		0.18	0.075	0.071	0.069	0.043
S		12	4.7	4.7	4.6	2.9

For the models using the continuous description of the density distribution (A, B, C), the c.o.m. of the deuterium scattering density is placed in 24(e) (0,0,z), $z = Z(D_3)/a_0$ ($a_0 = 10.382$ Å, space group $Fm3m$). The nitrogen position is determined *via* the ammonia geometry. $h(ND_3)$ is the distance between the c.o.m. of the D_3 group and the N atom. N atoms are located in 24(e) (0,0,z) with $z = [Z(D_3) - h(ND_3)]/a_0$. $\varrho(D_3)$ is the radius of the D_3 circle, which is in a plane perpendicular to [001]. For all models (A–D), the $\parallel$ components of the Debye–Waller factors are taken within this plane. The parameters used for the refinement of the split-molecule models (D, E) were chosen differently from the crystallographic convention, in order to match the parameters of models A–C as closely as possible. Instead of refining the atomic positions, we have determined the coordinates of the deuterium c.o.m. and the Euler angles describing the rotations and tilt of the ammonia molecule. This gives the deuterium c.o.m. in a general position: 192(l) (x,y,z), $x = X(D_3)/a_0$, $y = Y(D_3)/a_0$, $z = Z(D_3)/a_0$. With all Euler angles equal to zero, D1 is in 192(l) (x_1, y_1, z_1), $x_1 = [X(D_3) + \varrho(D_3)]/a_0$, $y_1 = Y(D_3)/a_0$, $z_1 = Z(D_3)/a_0$ and N in 192(l) (x,y,z), $x = X(D_3)/a_0$, $y = Y(D_3)/a_0$, $z = [Z(D_3) - h(ND_3)]/a_0$. For comparison, the atomic positions of model E are given:

Atom	Site	x	y	z
N	192(l)	−0.0110	0.0097	0.2058
D1	192(l)	0.0663	0.0566	0.2440
D2	192(l)	−0.0920	0.0594	0.2301
D3	192(l)	−0.0162	−0.0792	0.2472

$$R = \sum \Delta|F| / \sum |F|_{obs}; \qquad R_w = \left(\sum w\Delta|F|^2 / \sum w|F|_{obs}^2 \right)^{1/2}; \qquad S = R_w/R_{exp} \text{ with } R_{exp} = \left[(n - p) / \sum w|F|_{obs}^2 \right]^{1/2}.$$

The parameters determining the ammonia geometry, $h(ND_3)$ and $\varrho(D_3)$, show a remarkable independence of the different models. Compared with the values in Herzberg (1945), the molecule appears to be somewhat deformed, which means an $\sim 5\%$ decrease in $h(ND_3)$ and an insignificant ($\sim 1\%$) increase in $\varrho(D_3)$. A more pronounced deformation, but towards a prolate form, has been reported for the $Ca(ND_3)_6$ compound by Damay, Leclercq & Chieux (1990).

may be considered: they proposed a description of orientational disorder by sets of symmetry-related orientations. This concept may also be used for the description of RT coupling. One starts with a set of M equivalent displacement vectors, which are symmetry related (= 'split c.o.m. positions'). Corresponding to the local symmetry at one given displaced position, one or several (N) discrete molecular orientations may be introduced. The whole set of MN 'split molecules' is then generated by symmetry operations with an occupancy of one individual orientation $p = (MN)^{-1}$.

There is a clear disadvantage in this approach. Both the displacements $\mathbf{R}'$ and the orientations φ_{jk} are discrete

quantities. This, however, gives rise to relatively large Fourier components (Bragg intensity) for large Q, except if high values of M and N are taken. The transition to a continuous description, *e.g.* by introducing anisotropic Debye–Waller factors, unfortunately requires many additional parameters. On the other hand, even the most simplistic approach along the above lines provides a useful test of the calculations based on $\rho_{rot}(\mathbf{r}'|\mathbf{R})$. Also, the method can be used as an indication for introducing appropriate mechanistic or continuous models.

We have also followed an intermediate method. Discrete c.o.m. displacements $\mathbf{R}'$ are introduced but a continuous description by expanding into symmetry-adapted

functions is chosen for the orientational p.d.f. For a demonstration of the method, we again use the example of a triangular molecule of symmetry $3m$ at a site of symmetry $4mm$. For the sake of simplicity, instead of general displacement vectors only displacements along symmetry lines are considered. There are four equivalent vectors $\mathbf{R}'_1 = (\Delta, 0)$, $\mathbf{R}'_2 = (0, \Delta)$, $\mathbf{R}'_3 = (-\Delta, 0)$, $\mathbf{R}'_4 = (0, -\Delta)$; here Δ denotes the magnitude of the displacement of the molecular c.o.m. In the general case, there are eight such vectors. Now an expansion into symmetry-adapted surface functions is performed for each site with a displaced molecule. For site 1, $\rho(\varphi) \simeq (1 + c_3 \cos 3\varphi + c_6 \cos 6\varphi + \ldots)$ (mirror symmetry retained!). The contribution to the structure factor for this particular site then reads

$$f_1(Q_r, \varphi_q) = \tfrac{1}{4} \exp(iQ_r\Delta \cos \varphi_Q)[J_0(Q_r\varrho)$$
$$+ i^3 c_3 J_3(Q_r\varrho) \cos 3\varphi_Q$$
$$+ i^6 c_6 J_6(Q_r\varrho) \cos 6\varphi_Q + \ldots].$$

The other expressions are obtained after rotation by 90, 180 and 270°, respectively. Addition of these contributions yields, with the different orders l of $F_{\text{rot}}^{(l)}(\mathbf{Q})$ written down separately,

$$\tfrac{1}{2}J_0(Q_r\varrho)[\cos(Q_r\Delta \cos \varphi_Q) + \cos(Q_r\Delta \sin \varphi_Q)]$$
$$(l = 0)$$

$$\tfrac{1}{2}c_3 J_3(Q_r\varrho)[\cos 3\varphi_Q \sin(Q_r\Delta \cos \varphi_Q)$$
$$+ \sin 3\varphi_Q \sin(Q_r\Delta \sin \varphi_Q)] \qquad (l = 3)$$

etc. After expansion of the trigonometric functions into a series of Bessel functions and for small arguments Δ, exactly the same expressions as in § 2 are obtained. [Note: the $\sin 6\varphi_Q$ term in (4) is only obtained if general displacements are used.] Within this approach, only small displacements are considered. Therefore, the RT coupling enters *via* a product $c_3\Delta$, that is the product of a modulation amplitude and a displacement amplitude.

4. Example Ni(ND₃)₆Br₂

A comparison of different formulations of the structure factor is here applied in a practical case. The data are taken from a neutron diffraction experiment on an Ni(ND₃)₆Br₂ single crystal (Hoser, Prandl, Schiebel & Heger, 1990). The three D atoms are distributed at the corners of a square; this is a pronounced departure from the distribution that would be generated by an orientationally disordered ammonia molecule with absence of RT coupling. As discussed above, this would lead to a distribution on a circle with modulations of the order of 12 m. Rather than that, the p.d.f. reflects the fourfold site symmetry. In Hoser, Prandl, Schiebel & Heger (1990), a discussion of RT coupling is performed with a split-molecule approach and 26 parameters have been refined. We use the

data measured and analysed earlier [192 independent reflections, corrected for extinction; Hoser, Prandl, Schiebel & Heger, (1990)] in order to demonstrate the algorithms suggested in this paper, which need only 14 parameters at most. The estimated parameters for the different models are given in Table 1.

The first three models, A, B, C, use the continuous description of the density distribution. Sucessively higher expansion coefficients are taken into the refinement.

(A) A model describing orientational disorder, without RT coupling. The structure factor is calculated with $F_{\text{rot}}^{(0)} = J_0(Q_r\varrho)$ only, the next term is proportional to $J_{12}(Q_r\varrho) \cos(12\varphi_Q)$ and can be neglected. This model has the smallest number of parameters, ten, but yields a relatively poor $R_w = 0.18$.

(B) The same model with one additional parameter, $c_3^{(1)}$, describing RT coupling in lowest order:

$$F_{\text{rot}} = F_{\text{rot}}^{(0)} + F_{\text{rot}}^{(1)} = J_0(Q_r\varrho) + c_3^{(1)}\langle u^2 \rangle Q_r J_3(Q_r\varrho) \cos(4\varphi_Q).$$

The fourfold axis, as in the analysis of Hoser, Prandl, Schiebel & Heger (1990), is reflected by the $\cos(4\varphi_Q)$ term. Terms containing $J_9(Q_r\varrho)$ and Bessel functions of higher order are neglected. This additional parameter results in a reduction of R_w by a factor of more than two to 0.075. This is taken as evidence for the importance of RT coupling.

(C) Higher-order terms for the description of RT coupling are taken into the refinement:

$$F_{\text{rot}} = J_0(Q_r\varrho) + c_3^{(1)}\langle u^2 \rangle Q_r J_3(Q_r\varrho) \cos(4\varphi_Q)$$
$$- c_9^{(1)}\langle u^2 \rangle Q_r J_9(Q_r\varrho) \cos(8\varphi_Q)$$
$$+ \tfrac{1}{2}\langle u^2 \rangle^2 Q_r^2 J_6(Q_r\varrho)$$
$$\times [(c_{6,B1}^{(2)} + c_{6,B2}^{(2)}) \cos(4\varphi_Q)$$
$$+ (c_{6,B1}^{(2)} - c_{6,B2}^{(2)}) \cos(8\varphi_Q)]$$

but the three additional parameters yield only a slight improvement: $R_w = 0.071$. The fact that parameter $c_3^{(1)}$ remains unchanged underlines the significance and independence of this parameter.

So model B gives the most satisfactory result within the continuous description.

The next two models, D, E, use a discrete description of the density distribution. The eight locations of the '1/8 ND₃ molecules' are given by eight symmetry-related displacement vectors and the Euler angles.

(D) The motion of the ammonia molecule is described within the XY plane. Four parameters are required for the displacement vector and the orientation angle. This is the discrete equivalent to the continuous description of models A–C. With 13 parameters, an R_w of 0.069 is obtained, in agreement with the results of models B and C. As the N atoms are also subject to the translational displacements of the whole molecule, this additional disorder contribution is compensated by a reduction of $\langle u^2 \rangle_{N_\parallel}$.

(E) Leaving the main scope of the present paper, the motion of the ammonia molecule is described by five coordinates, allowing for a tumbling motion, similar to that given by Hoser, Prandl, Schiebel & Heger (1990): the axis of the ammonia molecule and the coordinate axis are no longer parallel. The intersection of the two axes is taken as a constraint into the fit, which couples the Euler angle φ to x and y. So with one additional parameter, R_w improves to 0.043. If the third Euler angle is also used as a parameter, R_w reduces to 0.040. But the φ and ψ are strongly correlated and therefore poorly defined, which is obviously linked to the small value of θ. The reduction of $\langle u^2 \rangle_{D_\perp}$ is explained analogously to the decrease of $\langle u^2 \rangle_{N_\parallel}$.

These results are in general agreement with those of Hoser, Prandl, Schiebel & Heger (1990). Finally, the model presented in §3, with discrete displacements and a continuous description for the orientational p.d.f. was refined. With 11 parameters, an R_w = 0.10 was obtained, which compares unfavourably with model B. As mentioned at the end of §3, the parameters c_3 and Δ are strongly correlated so only the product could be refined.

5. Concluding remarks

The structure factor calculated in §2 presents an alternative to the split-molecule approach. We have demonstrated that the two methods yield equivalent results in the case of planar motion. The continuous description emphasizes the physical origin of the p.d.f. but does not provide a direct visualization of the scattering density distribution. A p.d.f. map must be calculated for this purpose. One also has to be careful in interpreting the data of a split-molecule approach as the overlap of thermal ellipsoids suggests the calculation of a p.d.f. map in this case, too. The advantage of the continuous description lies in the possibility of increasing successively the number of parameters in the refinement and testing their relevance this way. This should be especially useful for data with limited information, as in the cases of a restricted 2θ range, crystal powder data or the presence of a large amount of disorder. As the example in this paper is based on high-quality single-crystal data with a large range in Q, the refinement requires more elaborate models.

The results of the split-molecule approach suggest an extension of the continuous distribution formulation from the planar to a more general curved motion. Unfortunately, it is not trivial to formulate structure factors that include this aspect. The problem is analogous to the generalization of an ellipsoid-shaped p.d.f., representative for a harmonic motion to a 'bent' p.d.f. Either this is done by a generalization of the structure factor to a cumulant expansion or by an additional factor, which consists of a power series in the components of Q. In both cases, symmetry leads to a reduction of terms and, in both cases, the analytic connection to expressions for the p.d.f. has to be taken with caution (International Tables for X-ray Crystallography, 1974). Unfortunately, a direct Fourier transform of a 'bent' p.d.f. (e.g. harmonic motion in an angular variable) is not available. Alternatively, one can start with a rigid ND_3 group that moves on a spherical surface. A structure factor is obtained by expanding into symmetry-adapted surface harmonics within the molecular frame and then transforming to the crystal frame, where a corresponding distribution function introduces both the tumbling of the dipolar axis and the rotation around this axis. While it is rather straightforward to formulate such a structure factor, there are too many parameters involved when the only restriction imposed is symmetry. Hence, it is necessary to calculate the expansion coefficients as a function of the parameters of a mechanistic model. While this is rather tedious work, a comparatively simple case without RT coupling that can be found in Bée (1988) sketches the approach.

An alternative way to analyse RT coupling was used by Schiebel, Hoser, Prandl & Heger (1990): the disordered density is first separated from the total scattering density of the crystal by Fourier methods. Then it is interpreted in terms of a model that introduces the potential at the crystal sites via a Boltzmann factor.

APPENDIX
Formal development

Obviously, both the molecular symmetry and the site symmetry determine which coefficients in an expansion into trigonometric functions contribute. In order to demonstrate the effect of the molecular symmetry, we follow exactly the same strategy as Press & Hüller (1973): a primed molecular frame (φ') rotating with the molecule and an unprimed crystal frame (φ) are introduced. An expansion of the angular part of the scattering-length density $g(\varphi')$ in the molecular frame (equilateral triangle) only yields terms of an order that conforms with the symmetry of the molecule. Therefore, only c_m with $m = 3l$ are nonzero and

$$g(\varphi') = \sum_{l=0}^{\infty} c_{3l} \exp(i3l\varphi') + c_{-3l} \exp(-i3l\varphi')$$

$$= \sum_{l=0}^{\infty} b_{3l} \cos(3l\varphi'), \tag{6}$$

where

$$c_{3l} = c_{-3l} = b_{3l}/2$$

is given by the mirror symmetry. The expansion coefficients can easily be determined:

$$c_{3l} = (1/2\pi) \int_0^{2\pi} g(\varphi') \exp(i3l\varphi') d\varphi'. \tag{7}$$

The transformation to the crystal frame is very simple in the 2D case: $\varphi' = \varphi - \Delta\varphi$ and, obviously, $\exp(il\varphi) = \exp(il\varphi')\exp(il\Delta\varphi)$. One can now express the angular part of the scattering-length density for neutron or X-ray scattering in the unprimed crystal frame:

$$g(\varphi) = \frac{1}{2}\sum_{l=0}^{\infty} b_{3l}[\exp(i3l\varphi - i3l\Delta\varphi)$$
$$+ \exp(-i3l\varphi + i3l\Delta\varphi)]. \tag{8}$$

The orientational distribution of the molecule is introduced by a distribution function $f(\Delta\varphi)$ and the angular part of the p.d.f. in the crystal frame is expressed as the convolution

$$a(\varphi) = (1/2\pi)\int_0^{2\pi} g(\varphi)f(\Delta\tilde{\varphi})d(\Delta\tilde{\varphi}), \tag{9}$$

where $f(\Delta\varphi)$ can be expanded into a Fourier series

$$f(\Delta\varphi) = \sum_{k=0}^{\infty} A_k \exp(ik\Delta\varphi) + A_{-k}\exp(-ik\Delta\varphi). \tag{10}$$

Insertion of (8) and (10) into (9) and integration over $\Delta\varphi$ yields

$$a(\varphi) = \frac{1}{2}\sum_{l=0}^{\infty}[A_{3l}b_{3l}\exp(i3l\varphi) + A_{-3l}b_{3l}\exp(-i3l\varphi)]. \tag{11}$$

Immediate expansion of $a(\varphi)$ into trigonometric functions

gives

$$a(\varphi) = \sum_{l=0}^{\infty}[a_l \exp(i3l\varphi) + a_{-l}\exp(-i3l\varphi)] \tag{12}$$

and, therefore,

$$a_l = \frac{1}{2}A_{3l}b_{3l}. \tag{13}$$

Hence, only terms of the same order $3l$ appear. This is also true in the presence of RT coupling, that is in the terms $\rho_{\text{rot}}^{(1)}, \rho_{\text{rot}}^{(2)}, \ldots$, introduced in the paper.

References

Bée, M. (1988). *Quasielastic Neutron Scattering*, ch. 7, and references therein. Bristol: Adam Hilger.

Damay, P., Leclercq, F. & Chieux, P. (1990). *Phys. Rev. B*, **41**, 9676–9682.

Guthrie, G. & McCullough, J. (1961). *J. Phys. Chem. Solids*, **18**, 53–61.

Herzberg, G. (1945). *Molecular Spectra and Molecular Structure*. II. *Infrared and Raman Spectra of Polyatomic Molecules*, p. 439. New York: Van Nostrand Reinhold.

Hohlwein, D. (1984). *Z. Kristallogr.* **169**, 237–247.

Hoser, A., Prandl, W., Schiebel, P. & Heger, G. (1990). *Z. Phys.* **81**, 259–263.

International Tables for X-ray Crystallography (1974). Vol. IV, edited by J. A. Ibers & W. C. Hamilton, ch. 5, subsections 5.2.3.1 and 5.2.3.2, and references therein. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Lax, M. (1974). *Symmetry Principles in Solid State and Molecular Physics*. New York: Wiley.

Press, W., Grimm, H. & Hüller, A. (1979). *Acta Cryst.* A**35**, 881–885.

Press, W. & Hüller, A. (1973). *Acta Cryst.* A**29**, 252–256.

Schiebel, P., Hoser, A., Prandl, W. & Heger, G. (1990). *Z. Phys.* **81**, 253–258.