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The probability distribution of X-ray intensities: the effect of one heavy atom in a triclinic cell containing a number of light atoms.

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1. Introduction

The rubidium and potassium acid salts,

$$M\mathrm{H}(o\text{-}\mathrm{NO_2}.\mathrm{C_6H_4}.\mathrm{COO})_2\,,$$

of *o*-nitrobenzoic acid have been shown recently (Speakman, 1957) to be triclinic with one molecule in the unit cell. Although the structure analysis is being successfully carried out on the basis of the centrosymmetric space group $P\bar{1}$, a statistical survey of the intensity data gave $N(z)$ distributions (Howells, Phillips & Rogers, 1950) suggesting that the correct space group is $P1$.

The effect on the theoretical $N(z)$ distributions of heavy atoms in fixed positions has been discussed by Collin (1955), but while his analysis is correct for the centric case, it appears to be incorrect for the acentric case and, moreover, no tables of numerical results are given.

The subject has accordingly been re-investigated and theoretical $N(z)$ curves for a triclinic cell containing one heavy atom (H) and a number of light atoms (L) have been calculated in terms of the parameter r defined by

$$r = f_H/(\Sigma_L)^{\frac{1}{2}}\,,$$

where

$$\Sigma_L = \sum_{i=1}^{m} f_i^2$$

is a summation over the m light atoms in the unit cell. The curves so derived have been denoted by ${}_{\mathrm{max.}\,\bar{1}}N(z, r)$ in the centric case and ${}_{\mathrm{max.}\,1}N(z, r)$ in the acentric case.

When r is large both these distributions converge on the ${}_{\mathrm{max.}}N(z)$ distribution of Hargreaves (1955).

2. Acentric case

Let the origin be chosen on the heavy atom so that

$$F(hkl) = x+iy\,,$$

where

$$x = f_H+\sum_{i=1}^{m} f_i \cos 2\pi(hx_i+ky_i+lz_i)\,,$$

$$y = \sum_{i=1}^{m} f_i \sin 2\pi(hx_i+ky_i+lz_i)\,.$$

The joint probability of x lying between x and $x+dx$, and of y lying between y and $y+dy$ is

$$p(x, y)\,dx\,dy = (\pi\Sigma_L)^{-1} \exp\,[-(x-f_H)^2/\Sigma_L] \exp\,[-y^2/\Sigma_L]\,dx\,dy\,.$$

Transforming to polar co-ordinates $(|F|, \alpha)$, there is obtained

$$p(|F|, \alpha)\,d|F|\,d\alpha = |F|(\pi\Sigma_L)^{-1} \exp\,[-(|F|^2+f_H^2)/\Sigma_L] \times \exp\,[2\cos\alpha|F|f_H/\Sigma_L]\,d|F|\,d\alpha\,,$$

and, since

$$p(|F|)\,d|F| = \int_{-\pi}^{\pi} p(|F|, \alpha)\,d|F|\,d\alpha\,,$$

it follows that

$$p(|F|)\,d|F| = 2|F|(\Sigma_L)^{-1} \exp\,[-|F|^2+f_H^2)/\Sigma_L \times I_0(2f_H|F|/\Sigma_L)\,d|F|\,,$$

where $I_0(x)$ is the modified zero-order Bessel function (Watson, 1922, p. 77).

Now let

$$z = I/\langle I\rangle = |F|^2/(\Sigma_L+f_H^2)\,,$$

so that

$$p(z)\,dz = (1+r^2) \exp\,[-\{(1+r^2)z+r^2\}] \times I_0[2r(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}]\,dz\,,$$

and

$${}_{\mathrm{max.}\,1}N(z, r) = \int_0^z p(z)\,dz = (1+r^2) \exp\,(-r^2) \times \int_0^z \exp\,[-(1+r^2)z]\,I_0[2r(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}]\,dz\,.$$

Table 1. *Values of* (*a*) ${}_{\mathrm{max.}\,1}N(z, r)$ *and* (*b*) ${}_{\mathrm{max.}\,\bar{1}}N(z, r)$

	(*a*)					(*b*)				
z/r	0	1	2	3	4	0	1	2	3	4
0·0	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·1	0·095	0·073	0·016	0·001	0·000	0·248	0·216	0·095	0·023	0·004
0·2	0·181	0·145	0·047	0·008	0·001	0·345	0·305	0·157	0·056	0·016
0·3	0·259	0·215	0·092	0·026	0·005	0·416	0·373	0·218	0·102	0·041
0·4	0·330	0·282	0·148	0·059	0·019	0·473	0·429	0·279	0·159	0·082
0·5	0·394	0·346	0·213	0·112	0·051	0·521	0·477	0·337	0·222	0·139
0·6	0·451	0·406	0·283	0·181	0·108	0·561	0·520	0·394	0·291	0·210
0·7	0·503	0·462	0·356	0·265	0·191	0·597	0·558	0·449	0·362	0·291
0·8	0·551	0·513	0·428	0·358	0·297	0·629	0·593	0·500	0·432	0·377
0·9	0·593	0·562	0·499	0·453	0·415	0·657	0·624	0·548	0·500	0·465
1·0	0·632	0·606	0·565	0·545	0·535	0·683	0·653	0·593	0·564	0·549
1·1	0·667	0·646	0·626	0·631	0·645	0·706	0·679	0·635	0·624	0·627
1·2	0·699	0·683	0·682	0·707	0·741	0·727	0·703	0·673	0·679	0·697
1·3	0·728	0·717	0·732	0·773	0·818	0·746	0·725	0·709	0·728	0·758
1·4	0·753	0·747	0·776	0·827	0·877	0·763	0·746	0·741	0·771	0·810
1·5	0·777	0·775	0·814	0·871	0·920	0·779	0·765	0·770	0·809	0·853

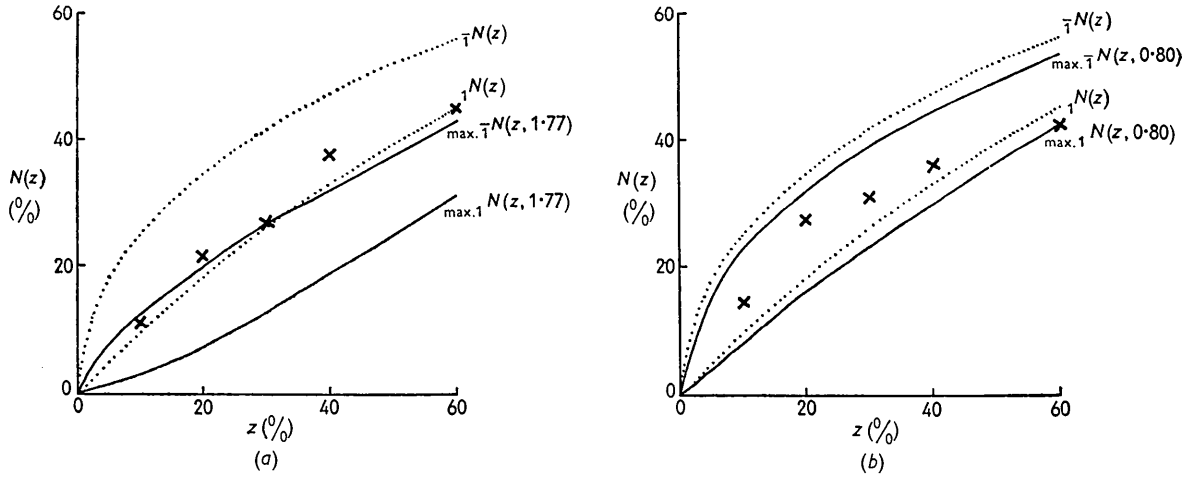

Fig. 1. (*a*) Comparison of the experimental distribution $N(z)$ for rubidium hydrogen di-*o*-nitrobenzoate (marked by crosses) with the theoretical distributions, $_1N(z)$, $\bar{1}N(z)$, $_{\text{max.}1}N(z, 1{\cdot}77)$ and $_{\text{max.}}\bar{1}N(z, 1{\cdot}77)$. (*b*) Comparison of the experimental distribution $N(z)$ for potassium hydrogen di-*o*-nitrobenzoate (marked by crosses) with the theoretical distributions $_1N(z)$, $\bar{1}N(z)$, $_{\text{max.}1}N(z, 0{\cdot}80)$ and $_{\text{max.}}\bar{1}N(z, 0{\cdot}80)$.

Values of $_{\text{max.}1}N(z, r)$ obtained by numerical integration are listed in Table 1(*a*).

The form of $_{\text{max.}1}N(z, r)$ when r is large can be seen by expressing $p(z)$ in the form

$$p(z) = (1+r^2)\exp\left[-\{(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}-r\}^2\right] \times I_0(2x^{\frac{1}{2}})\exp(-2x^{\frac{1}{2}}),$$

where

$$x = r^2(1+r^2)z .$$

For large x

$$I_0(2x^{\frac{1}{2}})\exp(-2x^{\frac{1}{2}}) \approx \tfrac{1}{2}\pi^{-\frac{1}{2}}x^{-\frac{1}{4}},$$

which varies only slowly with x, so that the behaviour of $p(z)$ depends largely on the function

$$\exp\left[-\{(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}-r\}^2\right],$$

which for large r has a sharp maximum at $z \approx 1$.

As $r \to \infty$, $p(z) \to 0$ for all $z > 0$ except $z = 1$, and

$$_{\text{max.}1}N(z, \infty) = 0, \quad 0 \le z < 1,$$
$$_{\text{max.}1}N(z, \infty) = 1, \quad z \ge 1,$$

which is the result given by Hargreaves (1955).

3. Centric case

$$p(|F|)d|F| = (2\pi\Sigma_L)^{-\frac{1}{2}}\{\exp\left[-(|F|-f_H)^2/2\Sigma_L\right] + \exp\left[-(|F|+f_H)^2/2\Sigma_L\right]\}d|F| .$$

Substitute

$$z = |F|^2/(\Sigma_L+f_H^2),$$

so that

$$p(z)dz = \tfrac{1}{2}\{(1+r^2)/2\pi z\}^{\frac{1}{2}}\{\exp\left[-\{(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}-r\}^2/2\right] + \exp\left[-\{(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}+r\}^2/2\right]\}dz ,$$

and

$$_{\text{max.}}\bar{1}N(z, r) = \varphi[(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}-r]+\varphi[(1+r^2)^{\frac{1}{2}}z^{\frac{1}{2}}+r],$$

where

$$\varphi(x) = (2\pi)^{-\frac{1}{2}}\int_0^x \exp(-\tfrac{1}{2}t^2)dt .$$

This expression is a simple modification of Collin's equation (12).

Values of $_{\text{max.}}\bar{1}N(z, r)$ are given in Table 1(*b*).

4. Discussion

Since the parameter r varies with the Bragg angle θ, a suitable average value must be used, and in the case of the rubidium and potassium acid salts of *o*-nitrobenzoic acid the values of r at $\sin\theta = 0{\cdot}45$ were used. For the rubidium salt r is 1·77 while for the potassium salt it is 0·80. Theoretical $_{\text{max.}}\bar{1}N(z, r)$ and $_{\text{max.}1}N(z, r)$ curves were obtained by interpolation in Table 1 and are compared in Fig. 1 with the experimental distributions and the $\bar{1}N(z)$ and $_1N(z)$ curves of Howells *et al.* (1950).

The experimental points (supplied by Dr Speakman) were evaluated for only the lower region of the $N(z)$ distribution, since this is the region of most importance for the detection of a centre of symmetry.

The results are in reasonable agreement with the assignment of $P\bar{1}$ as the space group, especially as it is felt that the data for the rubidium salt are the more reliable (Speakman, 1957).

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