Acta Cryst. (1951). **4**, 289

The Crystal Structure of Orthorhombic Hydrazonium Sulphate

By Isamu Nitta, Kiichi Sakurai and Yujiro Tomiie

Department of Chemistry, Osaka University, Nakanoshima, Osaka, Japan

(*Received* 16 *August* 1950)

Crystalline hydrazonium sulphate exists in two modifications, one orthorhombic and the other monoclinic. The crystal structure of the orthorhombic modification has been determined by the Laue and the rotating-crystal methods. The unit cell, containing four units of the chemical formula, has $a=8{\cdot}251$, $b=9{\cdot}159$, $c=5{\cdot}532$ A. The space group is D_2^4–$P2_12_12_1$. The atomic co-ordinates were determined by means of Patterson–Harker diagrams and two-dimensional Fourier syntheses. The sulphate group has the configuration of a nearly regular tetrahedron with the S–O distances 1·48–1·49 A. The O–O distances between different sulphate groups are greater than 3 A. The hydrazonium ion may be considered to be of the *trans* type, the N–N distance being 1·40 A. One of its nitrogen atoms forms three hydrogen bonds with the N–H...O distances 2·73 (two) and 2·77 A., and the other may be regarded as forming three bifurcated hydrogen bonds with the distances 2·79–2·99 A. Besides the oxygen atoms linked by the hydrogen bonds, each $N_2H_6^{++}$ group has three more oxygen neighbours, the total number of oxygen neighbours surrounding an $N_2H_6^{++}$ group being eleven.

Introduction

Hydrazine forms two kinds of salts in which it exists either as $N_2H_5^+$ or $N_2H_6^{++}$. For the present we shall call the former the hydrazinium and the latter the hydrazonium ion. Among the salts, only two, namely hydrazonium fluoride, $N_2H_6F_2$ (Kronberg & Harker, 1942), and hydrazonium chloride, $N_2H_6Cl_2$ (Wyckoff, 1923; Donohue & Lipscomb, 1947), have hitherto been examined by X-ray methods. It is the purpose of the present investigation to obtain some further information about the nature and structure of hydrazine salts.

Crystalline hydrazonium sulphate exists in two modifications (Groth, 1906–19), one orthorhombic and the other monoclinic; the former is dealt with here.

Preparation of crystals

Single crystals used in the structure analysis were obtained by allowing a saturated aqueous solution to evaporate slowly at room temperature. They are flat in shape a few millimetres square. We observed not infrequently that the orthorhombic crystals were accompanied by the monoclinic ones in the same solution. However, the latter were easily distinguished from the former by the form, and also by their readiness to become opaque. Our goniometric measurements showed the crystals obtained to be of class D_2–222 with the axial ratios $a:b:c=0{\cdot}9012:1:0{\cdot}6040$ and to cleave perfectly on {100}. The above value of the axial ratios is in good accord with that given by Groth (1906–19).

Unit cell and space group

Laue photographs taken with the X-ray beam parallel to the crystallographic axes showed the symmetry D_{2h}–*mmm*. Complete sets of oscillation photographs about the *a*, *b* and *c* axes taken with filtered Cu $K\alpha$ radiation were indexed in the usual manner. The dimensions of the unit cell were obtained from these photographs, and more accurate values were determined by the back-reflexion method, using (4.11.0), (207) and (10.0.2) spectra. They were

$$a=8{\cdot}251\pm0{\cdot}005,\ b=9{\cdot}159\pm0{\cdot}001,\ c=5{\cdot}532\pm0{\cdot}001\ \text{A.},$$

giving the axial ratios $a:b:c=0{\cdot}9009:1:0{\cdot}6039$, also in good agreement with the above goniometric values.

From the size of the unit cell and the density, 2·016 g.cm.$^{-3}$, determined at 7° C. by the pyknometer method, the number of the formula units in the unit cell was calculated to be four. No regular absences of reflexions other than (h00), (0k0), (00l) with h, k, and l odd respectively were observed, thus giving D_2^4–$P2_12_12_1$ as the space group.

Determination of the structure

Since, on inspection of a few preliminary oscillation photographs, the crystals showed a considerable extinction effect, their surfaces were ground with emery powder to eliminate it. In this way, it was possible to obtain good crystals for the *c*-axis photographs. But the extinction effect could not be eliminated completely from the specimens for the photographs around the *a* and *b* axes. Suitable corrections were therefore necessary for the strong reflexions of (0kl) and (h0l), the effect being more pronounced for the latter zone. The cross-sections of the rod specimens were 0·19 × 0·19 mm. for the [100], 0·25 × 0·30 mm. for the [010], and 0·15 × 0·38 mm. for the [001] photographs respectively. The intensities of reflexions were estimated by means of a microphotometer. Structure factors were deduced from these intensity data in the usual way. As the crystals were very thin, the absorption correction was assumed to be negligibly small.

For the space group D_2^4–$P2_12_12_1$, there exists only one set of positions, the general four-fold positions:

4 (a) x, y, z; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$. Disregarding the hydrogen atoms, there are then twenty-one parameters to be determined: three for each of the atoms S, O_I, O_{II}, O_{III}, O_{IV}, N_I and N_{II}.

As the first step in the structure determination, ordinary Patterson projections on (001) and (010) were made, using the ($hk0$) and the ($h0l$) data respectively. However, as both of them were found difficult to interpret, refined Patterson projections on these planes, with peaks sharpened, were then calculated from the formula

$$P'(x, y) = \sum_h \sum_k |F(hk0)/\bar{f}|^2 \cos 2\pi(hx+ky),$$

where $$\bar{f} = \sum_r f_r / \sum Z_r,$$

for the (001) projection, and from the similar formula for the (010) projection, Z_r and f_r being the number of electrons and the atomic scattering factor for the rth atom respectively. Although the peaks were made somewhat clearer, they were still not sufficiently resolved to permit an unambiguous interpretation. Two Harker functions, $H(x, y, \frac{1}{2})$ and $H(x, \frac{1}{2}, z)$, making use of the two-fold screw axes parallel to the z and y axes respectively, were calculated as the next step. From the Harker and the sharpened Patterson maps, approximate parameters for the S, O_I, O_{II}, O_{III} and O_{IV} atoms could then be determined, while those for N_I and N_{II} remained unfixed. The values obtained for the parameters also explained the peaks of the three-dimensional Patterson functions along the lines parallel to the c axis and passing through several peaks in the sharpened Patterson map $P'(x, y)$. It was then possible to proceed to make Fourier projections of the electron density on (001), (100) and (010), using the values of those structure factors whose signs were determined unambiguously by the contributions of the sulphur and the oxygen atoms only. By the method of successive approximation the final projections including all observed F's were obtained (Figs. 1, 2 and 3).

The atomic parameters (Table 1) determined in this way were finally adjusted by small amounts to obtain the best agreement between the observed and calculated F's.

Table 1. *Final atomic parameters*

	x	y	z
S	−0·0450	0·0677	0·2181
O_I	0·0618	0·0860	0·0033
O_{II}	0·0320	0·0723	0·4600
O_{III}	−0·1625	0·1917	0·2144
O_{IV}	−0·1290	−0·0750	0·1917
N_I	−0·0020	0·3340	0·7450
N_{II}	−0·1655	0·3173	0·6800

In calculating the structure factors the atomic scattering factors used for sulphur and oxygen were those of S^{+6} and O^{--} listed in the *Internationale Tabellen*, and the factors for $-NH_3^+$ group were taken equal to those for N plus the difference between those of O^{--} and O. The effect of thermal motion was taken into account by multiplying the calculated F values by a temperature factor $\exp[-B(\sin\theta/\lambda)^2]$, where $B = 0{\cdot}4$ A.^{2} The values of $R = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ are 0·17, 0·21 and 0·27 for ($0kl$), ($hk0$) and ($h0l$) zones respectively. The larger value of R for the ($h0l$) zones may be attributed to the less accurate intensity values due to appreciable extinction effect.

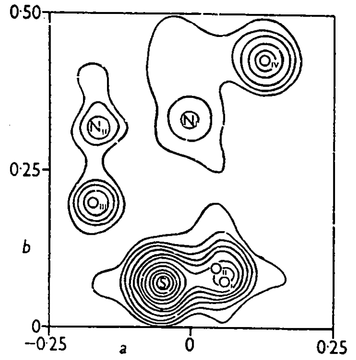

Fig. 1. Fourier projection of the electron density on (001). The contour lines are drawn on an arbitrary scale.

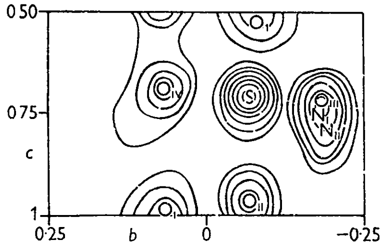

Fig. 2. Fourier projection of the electron density on (100). The contour lines are drawn on an arbitrary scale.

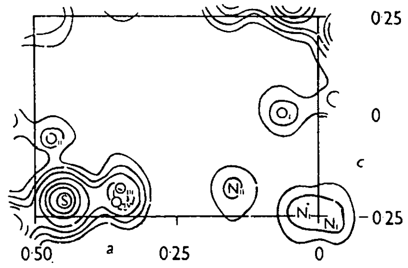

Fig. 3. Fourier projection of the electron density on (010). The contour lines are drawn on an arbitrary scale.

Discussion of the structure

The interatomic distances calculated from the parameter values (Table 1) are given in Table 2. The errors of these distances should not exceed 0·04 A. The projections of the structure on (001), (100) and (010) are shown in Figs. 4, 5 and 6.

The sulphate groups in the unit cell are all structurally equivalent. The S–O distances of the group are 1·48 and

1·49 A. These values are somewhat shorter than the generally accepted value 1·51 A. (Pauling, 1940). The O–O distances within it lie in the range 2·37–2·54 A., bond angles of ∠ O–S–O from 106 to 117°, thus giving the group the configuration of an approximately regular tetrahedron. The O...O distances between different sulphate groups are all greater than 3 A., which is considerably longer than that usually expected for the O–H...O hydrogen bond. It is therefore unlikely that in this crystal there exist hydrogen bonds between oxygen atoms, as is frequently the case for acidic salts of oxygen acids (e.g. $NaHCO_3$, KH_2PO_4, etc.).

Table 2. *Interatomic distances*

S–O_I	1·49 A.	N_I...O_I (*A*)	2·73* A.
–O_{II}	1·48	...O_{II} (*A*)	2·89
–O_{III}	1·49	...O_{II} (*B*)	2·73*
–O_{IV}	1·49	...O_{IV} (*B*)	2·77*
O_I–O_{II}	2·54	...O_I (*B*)	2·78
–O_{III}	2·40	...O_{III} (*C*)	2·82
–O_{IV}	2·39	...O_{III} (*A*)	3·19
O_{II}–O_{III}	2·37	...O'_{III} (*A*)	3·47
–O_{IV}	2·41		
O_{III}–O_{IV}	2·47	N_{II}...O_{III} (*A*)	2·82 †
N_I–N_{II}	1·40	...O_{IV} (*D*)	2·79 †
O_I(*A*)...O_{II} (*A*)	3·02	...O_I (*C*)	2·99 †
...O_{IV} (*B*)	3·44	...O_I (*B*)	2·82 †
...O'_{IV} (*B*)	3·50	...O_{II} (*C*)	2·80 †
...O_{III} (*C*)	3·28	...O'_{III} (*A*)	3·17
...O_{II} (*D*)	3·73	...O_{II} (*A*)	3·03
O_{II}(*A*)...O_{III} (*B*)	3·54	...O_{IV} (*B*)	3·22
...O_{IV} (*D*)	3·56	...O_{II} (*B*)	3·26
O_{III}(*A*)...O_{IV} (*B*)	3·26	...O_I (*A*)	3·35
...O_{IV} (*D*)	3·33		
O_{IV}(*A*)...O_{IV} (*B*)	3·75		

* Normal hydrogen bond.
† Bifurcated hydrogen bond.

The value 1·40 A. obtained for the N–N distance is somewhat shorter than 1·42 A. found in $N_2H_6F_2$ (Kronberg & Harker, 1942) and $N_2H_6Cl_2$ (Donohue & Lipscomb, 1947). In both of these halides the cation has been found to be $N_2H_6^{++}$ of the minimum symmetry C_{3i}–$\bar{3}$, having thus the *trans* configuration. The same conclusion has been drawn from the consideration of the directions of hydrogen bonds. According to the experiments on the Raman effect, the frequencies of the N–N valence vibration for N_2H_4 in the liquid state (Kohlrausch, 1936), and for $N_2H_5^+$ and $N_2H_6^{++}$ in aqueous solutions (Edsall, 1937), are 876, 965 and 1036 cm.$^{-1}$ respectively. Considering these facts, it is concluded that the increase of the frequencies may be connected with the increase of the total charge of these groups. The N–N vibrations for crystalline $N_2H_6Cl_2$ and $N_2H_6SO_4$ are 1024 and 1050 cm.$^{-1}$ (Ananthakrishnan, 1937), both of which correspond to the above-mentioned frequency of $N_2H_6^{++}$; thus it is probable that the cation in crystalline $N_2H_6SO_4$ is in the state of $N_2H_6^{++}$. This is further supported by the fact that the N–N distance is 1·47 A. (Giguère & Schomaker, 1943) for the hydrazine molecule (in gaseous state), 1·44 A. for the $N_2H_5^+$ ion in hydrazinium chloride, N_2H_5Cl (Nitta, Sakurai & Tomiie, unpublished), and still smaller values 1·40–1·42 A. for $N_2H_6^{++}$. A detailed discussion of the structure of the $N_2H_6^{++}$ ion has been given by Kronberg & Harker (1942) in their investigation of the crystal structure of $N_2H_6F_2$. According to them, the shortening of the N–N distance of the $N_2H_6^{++}$ ion relative to that in the gaseous hydrazine molecule may be attributed to the so-called 'formal charge effect', the contribution of

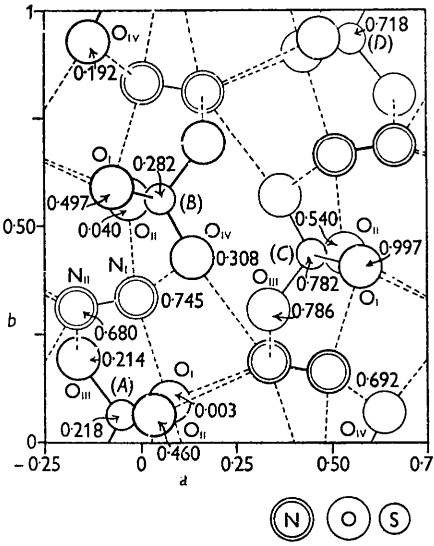

Fig. 4. The projection of the structure on (00$\bar{1}$). The solid lines represent chemical bonds and the broken lines hydrogen bonds. The numbers give the z parameters.

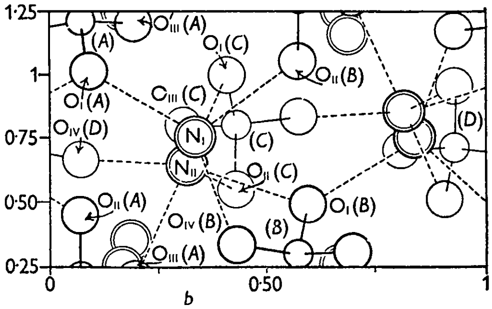

Fig. 5. The projection of the structure on (100). The solid lines represent chemical bonds and the broken lines hydrogen bonds.

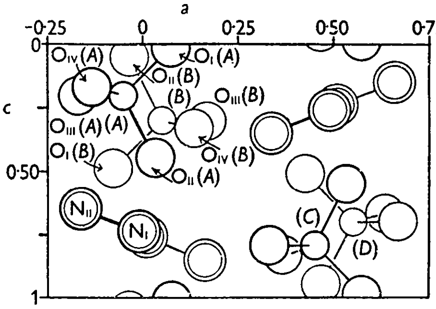

Fig. 6. The projection of the structure on (010). The solid lines represent chemical bonds and the broken lines hydrogen bonds.

the adjacent charge structure to the normal state of the ion being estimated to be 25 %. However, it does not seem possible that such a small percentage of the formal charge would cause a shortening of the bond distance as remarkable as that actually observed, following a discussion given by Donohue & Lipscomb (1947). On the other hand, it is to be noted that, according to Hughes & Lipscomb (1946), in the case of methylammonium chloride crystals investigated carefully by X-rays, the C–N bond distance does not apparently show the effect of shortening by the formal charge on the basis of Pauling's values for covalent radii. Therefore, it is desirable to consider what is the reason for the shortening of the N–N bond and to study the formal charge effect more thoroughly.

One of the nitrogen atoms, N_I, has three nearest oxygen neighbours, $O_I(A)$, $O_{II}(B)$ and $O_{IV}(B)$, the N...O distances being 2·73, 2·73 and 2·77 A. These N...O distances can be interpreted as those of hydrogen bonds. The environment of the other nitrogen atom, N_{II}, is somewhat complicated, $O_{III}(A)$ and $O_I(B)$ being both at 2·82 A., $O_{II}(C)$ at 2·80 A., $O_{IV}(D)$ at 2·79 A., and $O_I(C)$ at 2·99 A. The directions of the N–H bonds about N_{II} cannot be concluded so simply as in the case about N_I, but it may be considered that there are three bifurcated hydrogen bonds in the following manner:

$$N_{II}\begin{matrix}\cdot\cdot O_{III}(A)\\ \cdot\cdot O_{IV}(D)\end{matrix}\qquad N_{II}\begin{matrix}\cdot\cdot O_I\ (B)\\ \cdot\cdot O_{II}(C)\end{matrix}\qquad \text{and}\quad N_{II}\begin{matrix}\cdot\cdot O_I\ (C)\\ \cdot\cdot O_{IV}(D).\end{matrix}$$

In Fig. 7, the environment of one $N_2H_6^{++}$ group is projected upon two planes parallel and perpendicular to the N_I–N_{II} axis.

The hydrogen-bond distance, 2·73 A., is shorter than any so far found for N–H...O except for that of β-glycylglycine (Hughes & Moore, 1949). For the sake of comparison, reported values of N–H...O distances are given in Table 3.

$O_I(B)$ and $O_{III}(A)$, both already hydrogen-bonded to N_{II}, lie respectively at 2·78 and 3·19 A. from N_I, whereas $O_{II}(B)$ and $O_{IV}(B)$, also hydrogen-bonded to N_I, are at 3·26 and 3·22 A. from N_{II}. Besides the oxygen atoms held by the hydrogen bonds mentioned above, each $N_2H_6^{++}$ group has still three more oxygen neighbours, $O_{III}(C)$, $O_{II}(A)$ and $O'_{III}(A)$, which are linked by the electrostatic attraction to one or the other $-NH_3^+$ group. Thus each $N_2H_6^{++}$ group is surrounded by eleven oxygen atoms in all.

The existence of very strong N–H...O hydrogen bonds may be due to the increased ionic character of the N–H bonds as compared with that in the NH_4^+ group (Kronberg & Harker, 1942).

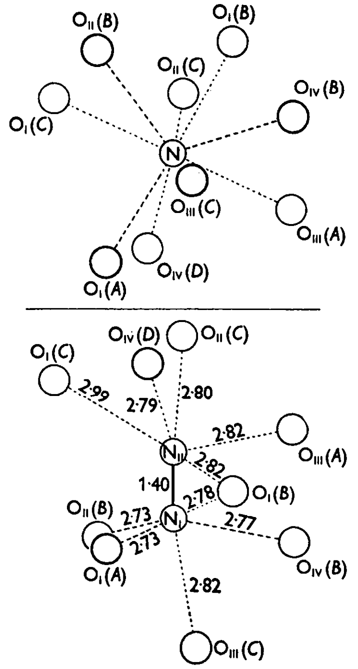

Fig. 7. The environment of one $N_2H_6^{++}$ group projected upon two planes parallel and perpendicular to the N_I–N_{II} axis. The interatomic distances are given in Ångström units.

In connexion with the structure of the $N_2H_6^{++}$ ion, it seems of interest to obtain information regarding the structure of $N_2H_5^+$ ion, and for this purpose we have analysed the crystal of hydrazinium chloride; the result will be published later.

In conclusion, the authors desire to express their thanks to the Department of Education for a grant.

References

Albrecht, G. & Corey, R. B. (1939). *J. Amer. Chem. Soc.* **61**, 1087.

Ananthakrishnan, R. (1937). *Proc. Indian Acad. Sci.* A, **5**, 76.

Corey, R. B. (1938). *J. Amer. Chem. Soc.* **60**, 1598.

Donohue, J. & Lipscomb, W. N. (1947). *J. Chem. Phys.* **15**, 115.

Table 3. N–H...O *distances*

$NH_4H_2PO_2$ (Zachariasen & Mooney, 1934)	2·81 A.
Urea (Wyckoff & Corey, 1934)	2·98, 3·03
$(NH_4)_2C_2O_4.H_2O$ (Hendricks & Jefferson, 1936)	2·76–2·88
Diketopiperazine (Corey, 1938)	2·85
Glycine (Albrecht & Corey, 1939)	2·76, 2·88 (for normal hydrogen bonds) 2·93, 3·05 (for a bifurcated hydrogen bond)
Acetamide (Senti & Harker, 1940)	2·86
DL-Alanine (Levy & Corey, 1941)	2·78, 2·84, 2·88
$CO(NH_2)_2.H_2O_2$ (Lu, Hughes & Giguère, 1941)	2·94, 3·04
$NH_4H_2PO_4$ (Ueda, 1948)	2·87
β-Glycylglycine (Hughes & Moore, 1949)	2·68, 2·80, 2·81

Edsall, J. T. (1937). *J. Chem. Phys.* **5**, 225.
Giguère, P. A. & Schomaker, V. (1943). *J. Amer. Chem. Soc.* **65**, 2025.
Groth, P. (1906–19). *Chemische Krystallographie.* Leipzig: Engelmann.
Hendricks, S. B. & Jefferson, M. E. (1936). *J. Chem. Phys.* **4**, 102.
Hughes, E. W. & Lipscomb, W. N. (1946). *J. Amer. Chem. Soc.* **68**, 1970.
Hughes, E. W. & Moore, W. J. (1949). *J. Amer. Chem. Soc.* **71**, 2618.
Kohlrausch, K. W. F. (1936). *Mh. Chem.* **68**, 349.
Kronberg, M. L. & Harker, D. (1942). *J. Chem. Phys.* **10**, 309.
Levy, H. A. & Corey, R. B. (1941). *J. Amer. Chem. Soc.* **63**, 2095.
Lu, Chia-Si, Hughes, E. W. & Giguère, P. A. (1941). *J. Amer. Chem. Soc.* **63**, 1507.
Pauling, L. (1940). *The Nature of the Chemical Bond*, 2nd ed. Ithaca: Cornell University Press.
Senti, F. & Harker, D. (1940). *J. Amer. Chem. Soc.* **62**, 2008.
Ueda, Ryuzo (1948). *J. Phys. Soc. Japan*, **3**, 328.
Wyckoff, R. W. G. (1923). *Amer. J. Sci.* **5**, 15.
Wyckoff, R. W. G. & Corey, R. B. (1934). *Z. Krystallogr.* **89**, 462.
Zachariasen, W. H. & Mooney, R. C. L. (1934). *J. Chem. Phys.* **2**, 34.

Acta Cryst. (1951). **4**, 293

Diffusion des Rayons X par les Fluides*

Par Gérard Fournet†

Office National d'Études et de Recherches Aéronautiques
Direction Matériaux, 25 Avenue de la Division-Leclerc, Chatillon s/Bagneux (Seine), France

(*Reçu le* 20 *septembre* 1950)

The intensity of radiation scattered in a medium has been expressed by Zernicke & Prins by means of a probability function $P(r)$ for finding two molecules at distance r; this function contains a purely geometrical description of the state of the system without attempting any explanation. We give here an expression for this intensity based on the kinetic theory of fluids of Born & Green; this expression contains the characteristic features of the molecular assemblage, namely, structure factor, intermolecular force potential, average volume per molecule, and temperature.

The theoretical and the experimental curves for the scattering by argon (gas and liquid) agree in all essential features.

1. Introduction

Le développement de l'étude de la diffusion des rayons X aux faibles angles par des solutions de grosses particules (molécules de protéines par exemple) a donné un nouvel intérêt aux théories de la diffusion des rayons X par les ensembles de particules. Le but de notre travail est l'étude de l'influence du rapprochement des particules sur la répartition du rayonnement diffusé en fonction de l'angle. Notre exposé principal sera limité au cas où les particules, toutes identiques, possèdent la symétrie sphérique.

La formule classique (Zernicke & Prins, 1927) de l'intensité I du rayonnement diffusé par un ensemble de N particules (contenues dans un volume V) en fonction de l'angle de diffusion 2θ est:

$$I(h)=I_e(h)\,NF^2(h)\left\{1-\frac{1}{v_1}\int_0^\infty[1-P(r)]\,\frac{\sin hr}{hr}\,4\pi r^2dr\right\}, \qquad (1)$$

$$I(h)=I_e(h)\,NF^2(h)\left\{1-\frac{v_2(h)}{v_1}\right\}, \qquad (1\,bis)$$

où h désigne le rapport $(4\pi\sin\theta)/\lambda$, $I_e(h)$ l'intensité diffusée par un éléctron, $F(h)$ le facteur de structure de chaque particule, et v_1 le volume moyen offert à chaque particule ($v_1=V/N$). La fonction de répartition $P(r)$ sert à définir la probabilité P de trouver *à la fois* le centre d'une particule dans un élément de volume dv_k, très petit devant les dimensions des particules, et le centre d'une *autre* particule dans un élément dv_j situé à une distance r de dv_k:

$$P=\frac{dv_k}{v_1}\,\frac{dv_j}{v_1}\,P(r).$$

Il est difficile d'étudier à partir de la formule (1) l'influence du rapprochement des particules sur la courbe de diffusion: quand la concentration de la matière augmente, v_1 diminue, mais on ne connaît pas *a priori* l'évolution de $P(r)$. Cette dernière fonction, inventée pour les besoins de la cause, ne fait que traduire un aspect géométrique de la réalité sans l'expliquer. Pour aller plus loin, il faut donc relier la fonction $P(r)$ à d'autres caractéristiques de la matière étudiée et substituer à l'expression géométrique de l'intensité (1) une expression 'thermodynamique'.

---

* Extrait du paragraphe 1·2·4 d'une thèse de Doctorat d'État présentée à la Faculté des Sciences de Paris: 'Étude théorique et expérimentale de la diffusion des Rayons X par les ensembles denses de particules' (Paris, 1950).

† Actuellement à Division Rayons X de l'O.N.E.R.A., Laboratoire du Professeur Guinier, Conservatoire National des Arts et Métiers, 292 Rue St Martin, Paris III, France.