THE THEORY OF OPTICAL ACTIVITY OF CRYSTALS

II. Calculation of the Rotatory Power of $NaClO_3$ and $NaBrO_3$

BY G. N. RAMACHANDRAN, F.A.Sc.

(*From the Department of Physics, Indian Institute of Science, Bangalore 3*)

1. INTRODUCTION

IN Part I, an account of the general theory has been given together with an example of the application of the theory to a hypothetical structure. In this part, it is proposed to apply the theory to calculate the values of rotatory power for two crystals of the cubic system, $NaClO_3$ and $NaBrO_3$. We shall retain the symbols used in Part I.

Both $NaClO_3$ and $NaBrO_3$ belong to the tetartohedral (T) class of the cubic system. Their structures have been determined by several workers (Dickinson and Goodhue, 1921; Kolkmeijer, Bijeovet and Karsson, 1921; Kiby, 1923; Zachariasen, 1929). All of them agree in placing the structure in the space-group T^4-P2_13 and in giving the number of molecules per unit cell as 4. The co-ordinates of the different atoms in one of the enantiomers are as follows with respect to a right-system of co-ordinates:

$4 \text{ Na} \qquad uuu; \quad \frac{1}{2}+u, \frac{1}{2}-u, \bar{u}; \quad \bar{u}, \frac{1}{2}+u, \frac{1}{2}-u; \quad \frac{1}{2}-u, \bar{u}, \frac{1}{2}+u$

$4 \text{ Cl (4 Br)} \quad vvv; \quad \text{etc.}$

$12 \text{ O} \qquad xyz; \quad \frac{1}{2}+x, \frac{1}{2}-y, \bar{z}; \quad \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; \quad \frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$

$\qquad\qquad\quad yzx; \quad \text{etc.}$

$\qquad\qquad\quad zxy; \quad \text{etc.}$

The different workers, however, give slightly different values for u, v, x, y, z. Of the various measurements, that of Zachariasen is the most accurate; but he has studied only $NaClO_3$. Consequently, Zachariasen's data are taken for this crystal, *viz.*, $u = 0\cdot064$, $v = 0\cdot417$, $x = 0\cdot303$, $y = 0\cdot592$, $z = 0\cdot500$ and lattice parameter $a = 6\cdot57$ Å. The data of Dickinson and Goodhue for $NaClO_3$ agree closely with this and therefore their measurements for $NaBrO_3$ have been used for our calculations. They are: $u = 0\cdot09$, $v = 0\cdot41$, $x = 0\cdot30$, $y = 0\cdot60$, $z = 0\cdot47$ and $a = 6\cdot71$ Å.

The unit cell is shown in Fig. 1, where the four O_3 groups have been labelled 1, 2, 3, 4 respectively. We shall first consider sodium chlorate.

2. CALCULATION OF THE POLARISABILITIES

From the refractive index ($n_D = 1 \cdot 514$) of sodium chlorate, the molar refraction of the compound is calculated to be $R = 12 \cdot 8$. Now, it is well known that the positive ion has a low molar refraction (Fajans and Joos, 1924; Pauling, 1927). For Na, this is of the order of $0 \cdot 5$. As regards ClO_3^- ion, no values are available in the literature for the contributions of Cl and O atoms separately. However, the following table for ions of the type AO_3 taken from the data in Fajans and Joos' paper is helpful. The table shows that the atom A in the ion AO_3 always has a small molar refraction.
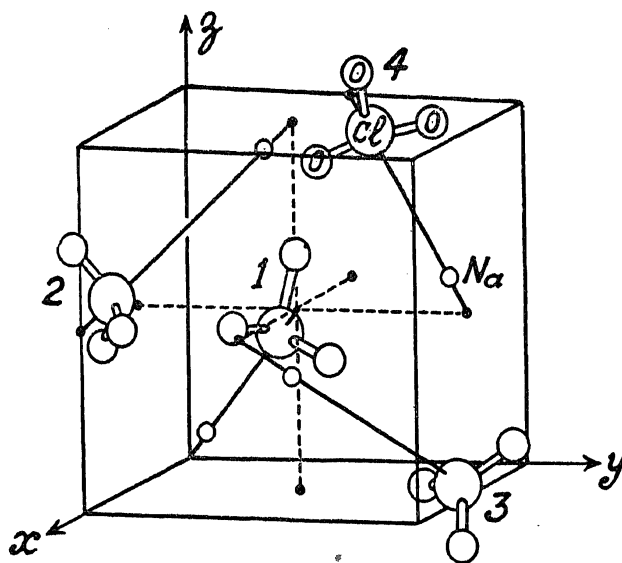

FIG. 1. Unit Cell of Sodium Chlorate

TABLE I

Ion		R_O	R_A
CO_3^{--}	..	4·08	0·03
SiO_3^{--}	..	4·42	0·10
NO_3^-	..	3·66	0·02
SO_3^{--}	,..	3·65	0·05
ClO_4^-	..	3·32	0·04

We may therefore choose similarly a low value $0 \cdot 05$ for the Cl atom in ClO_3. Thus, we may take $R_{Na} = 0 \cdot 45$, $R_{Cl} = 0 \cdot 05$, $R_O = 4 \cdot 1$, which lead to the value $12 \cdot 8$ for $NaClO_3$. This set of values is reasonable, since the value $4 \cdot 1$ for R_O is about the mean value found in different ions of the type AO_3, although

larger than in ClO_4. Using Heaviside units, we have the polarisability $\alpha = 3\,R/N$, where N is the Avogadro number. Thus,

$$\alpha_{Na} = 0 \cdot 22, \ \alpha_{Cl} = 0 \cdot 025, \ \alpha_0 = 2 \cdot 03 \times 10^{-23} \tag{1}$$

Now, in calculating the interactions of the different atoms in the structure, we may take the ClO_3 group as a unit. Further, since the Cl atoms contribute only about $\frac{1}{2}\%$ of the polarisability of this group, we may neglect them for convenience and consider only the O_3 group. Calculations from the structure show that the O_3 group is an equilateral triangle, the O—O distance (d) being $2 \cdot 38$ Å. Consequently, we may calculate the principal polarisabilities of this group, using the method of Bragg (1924). If $\alpha_{\perp}$ and $\alpha_{\shortparallel}$ are respectively the polarisabilities normal to the plane of the O_3 group and for directions in the plane, then their values are calculated to be

$$\alpha_{\perp} = 4 \cdot 92 \times 10^{-23}, \ \alpha_{\shortparallel} = 7 \cdot 14 \times 10^{-23}. \tag{2}$$

In the $NaClO_3$ structure, therefore, we may replace each set of 3 oxygen atoms by a single anisotropic group having the above components for the polarisability and situated at the centre of gravity of the triangle. The co-ordinates of the centres of gravity of the four O_3 groups, as well as the orientation of the normals to their planes, are indicated below:

1. w, w, w 2. $\frac{1}{2} + w, \frac{1}{2} - w, \bar{w}$ 3. $\bar{w}, \frac{1}{2} + w, \frac{1}{2} - w$ 4. $\frac{1}{2} - w, \bar{w}, \frac{1}{2} + w$

   [111]   [1$\bar{1}$1]   [1 1 $\bar{1}$]   [$\bar{1}$ 1 1]

with $w = 0 \cdot 465$.

We shall make a further simplification by neglecting all the sodium atoms also (since these contribute only about 4% to the total polarisability). Thus, for the purpose of our calculations, we are left with four anisotropic O_3 groups, 1 to 4, per unit cell.

It is convenient to take Ox, Oy, Oz along the cubic axes of the crystal. Since the O_3 groups all have their normals along one or the other of the four [[111]] axes, their polarisabilities α_{ij} referred to cubic axes can be described by two parameters $A = (\alpha_{\perp} + 2\alpha_{\shortparallel})/3$ and $B = (\alpha_{\perp} - \alpha_{\shortparallel})/3$. The components of the polarisability tensor for the four O_3 groups are given below:

Type 1			Type 2			Type 3			Type 4		
A	B	B	A	−B	−B	A	−B	B	A	B	−B
B	A	B	−B	A	B	−B	A	−B	B	A	−B
B	B	A	−B	B	A	B	−B	A	−B	−B	A

$$\tag{4}$$

Clearly, $A = 6 \cdot 40 \times 10^{-23}$ and $B = -0 \cdot 74 \times 10^{-23}$ (5)

3. Calculation of the Interaction of Neighbours

In the structure, each O_3 group is surrounded by twelve others (similar to the 12 next nearest neighbours of the same type in the NaCl structure). The co-ordinates of the twelve neighbours of group 1 are shown in Table II, taking that particular group as origin. These are divided into three sets of four each, all the groups in one set having the same orientation. Similar tables can be prepared for the neighbours of groups 2, 3 and 4.

TABLE II

Neighbours of O_3 Group 1

Type	Co-ordinates											
2	0·50,	−0·43,	0·07;	−0·50,	−0·43,	0·07;	0·50, 0·57, 0·07;	−0·50,	0·57,	0·07
3	0·07,	0·50,	−0·43;	0·07,	−0·50,	−0·43;	0·07, 0·50, 0·57;	0·07,	−0·50,	0·57
4	−0·43,	0·07,	0·50;	−0·43,	0·07,	−0·50;	0·57, 0·07, 0·50;	0·57,	0·07,	−0·50

Now consider light having its electric vector parallel to Ox being propagated along the positive z-axis. Then the phase of the wave at an atom (x, y, z) is exp. $(- kaz)$, since x, y, z are expressed as fractions of the unit cell dimension a. Since none of the components of the polarisability tensor are zero, all the four types of O_3 groups will have components of electric moment along Ox, Oy and Oz. Taking these into account, the induced fields F_x, F_y, F_z are calculated at each group. Each of these three components would produce an additional moment parallel to all three axes. In this way, the final induced moments μ_x and μ_y (taking into account the influence of neighbours) is calculated for all the four groups in the unit cell. Adding them up, we obtain

$$\sum_{1}^{4} \mu_{rx} = \left[25 \cdot 6 \times 10^{-23} - \frac{2}{\pi a^3} (0 \cdot 115\ A^2 + 0 \cdot 928\ AB + 8 \cdot 50\ B^2) \right] \left(E_x + \frac{P_x}{3} \right) \quad (6)$$

$$\sum_{1}^{4} \mu_{ry} = i \frac{2}{\pi a^3} (0 \cdot 100\ AB + 3 \cdot 096\ B^2)\ ka \left(E_x + \frac{P_x}{3} \right) \quad (7)$$

Since λ in the medium is λ_0/n, where $\lambda_0 = 5 \cdot 893 \times 10^{-5}$ for the sodium D line, we have

$$P_x = 0 \cdot 9042\ (E_x + P_x/3); \quad P_y = 0 \cdot 685 \times 10^{-5} n\ (E_x + P_x/3) \quad (8)$$

From these, we obtain $n = 1 \cdot 514$ and $g/n = 9 \cdot 806 \times 10^{-6}$. Thus

$$\rho = \frac{\pi}{\lambda_0} \cdot \frac{g}{n} = 30° \cdot 0 \text{ per cm.}$$

This compares well with the experimentally observed value of $31°\cdot3$. The excellent agreement between the two must be considered to be fortuitous. In fact, small changes in the parameters used would lead to an appreciable alteration in the value of the rotatory power. It is however interesting to note that the theory gives the right order of magnitude.

4. ROTATORY POWER OF SODIUM CHLORATE IN THE ULTRA-VIOLET

Calculations similar to the above can readily be made in the ultra-violet if the polarisabilities of the individual atoms are known. Unfortunately, all studies on molar refraction, etc., have been confined to a single wavelength, *viz.*, the D line and no data are available in the literature for the ultra-violet. However, an approximate estimate can be made as shown below. We consider the wavelength $\lambda_0 = 2573$ Å for which the rotatory power of $NaClO_3$ has been measured by Rose (1909). The refractive index for this wavelength is $1\cdot585$, so that the calculated molar refraction is $14\cdot3$. This has to be divided into the separate contributions of Na, Cl and O. It would not be correct to divide them in the same ratio as for $\lambda\, 5893$ since oxygen would have a smaller dispersion than the other two. A reasonable estimate is as follows:

$$R_{Na} = 1\cdot0, \quad R_{Cl} = 0\cdot1, \quad R_O = 4\cdot4.$$

Naturally, there is a certain amount of uncertainty in these estimates, but they enable us to calculate the order of magnitude of ρ. These lead to $a_{Na} = 0\cdot50$, $a_{Cl} = 0\cdot05$ and $a_O = 2\cdot17$, $\times 10^{-23}$, from which we have

$$a_{\parallel} = 2\cdot59, \quad a_{\perp} = 1\cdot73, \quad A = 6\cdot91, \quad B = -0\cdot86, \times 10^{-23}.$$

Substituting in equations (6) and (7) and making the calculations just as for $\lambda\, 5893$, one finds $\rho = 226°$, as compared with the value $147°\cdot3$ found experimentally. It is interesting to note that the order of magnitude is correct.

5. CALCULATIONS FOR SODIUM BROMATE

Rose (*loc. cit.*) has also measured the optical rotatory power of $NaBrO_3$ from 4000 to 7500 Å and we give below his data for two wavelengths near the upper and lower limits:

λ_o	n	ρ
7188	$1\cdot610$	$13°\cdot9$
4047	$1\cdot643$	$72°\cdot0$

Taking 7,188 first, the value of R_{NaBrO3} is calculated to be $15\cdot0$. There appear to be no data in the literature as to the individual values of R_{Br} and R_O in the bromate ion. We, therefore, make the following estimates.

$$R_{Na} = 0\cdot5, \quad R_{Br} = 0\cdot7, \quad R_O = 4\cdot6.$$

R_{Na} is the same as in $NaClO_3$. Since Br is a much larger atom than Cl, we have taken R_{Br} to be fairly large. R_O has a value larger than in ClO_3, but we cannot reduce it further without abnormally increasing R_{Br}. The above values lead to $a_{||} = 2 \cdot 66 \times 10^{-23}$ and $a_{\perp} = 1 \cdot 86 \times 10^{-23}$ for the O_3 group. If we take the co-ordinates of Dickinson and Goodhue (*loc. cit.*) for the atoms in the unit cell of $NaBrO_3$, the O—O distance is $2 \cdot 51$ Å and the centres of gravity of the O_3 groups occur at w, w, w, etc., where $w = 0 \cdot 46$. This value of w is close to the value $0 \cdot 465$ in $NaClO_3$, so that we may take the latter here also and no detailed calculations need be made, except to put in the appropriate values of the polarisabilities in equations (6) and (7). As in $NaClO_3$, here also we neglect the effects of Na and Br, as they contribute only about 8% to the total polarisability. It is calculated that $A = 7 \cdot 18 \times 10^{-23}$ and $B = -0 \cdot 80 \times 10^{-23}$ and with these ρ is found to be equal to $22 \cdot 1°$ for $\lambda 7188$.

Taking 4047, R_{NaBrO3} is $15 \cdot 65$. Obviously, the molar refraction of oxygen would vary very little from $\lambda 7188$ to $\lambda 4047$, since oxygen has a dispersion frequency in the remote ultra-violet. Further, most of the dispersion must be due to bromine, since $NaBrO_3$ absorbs light completely below 4000 Å, while $NaClO_3$ does so only below 2200 Å. Hence, we estimate the contributions of the different atoms as follows:

$$R_{Na} = 0 \cdot 6, \quad R_{Br} = 1 \cdot 0, \quad R_O = 4 \cdot 65.$$

Thus $A = 7 \cdot 21 \times 10^{-23}$, $B = -0 \cdot 80 \times 10^{-23}$ and ρ is calculated to be 71° for $\lambda 4047$.

6. DISCUSSION OF THE RESULTS

The calculated and the experimental values of ρ for the two crystals are shown in Table III.

TABLE III

	$NaClO_3$			$NaBrO_3$	
	ρ (th)	ρ (exp.)		ρ (th)	ρ (exp.)
5893	30°·0	31°·3	7188	22°·1	13°·9
2573	226°	147°·3	4047	71°·0	72°·0

The agreement should be considered satisfactory, since the values for the polarisabilities are not very accurate.

The structure of $NaClO_3$ can be considered to be derived from the NaCl structure by a slight distortion in which both the anions and cations

are displaced parallel to the body diagonals. If the O_3 groups considered above occupy exactly the points of a face centred lattice (like the Cl's in NaCl), *i.e.*, $w = 0 \cdot 50$ in (3), then the rotation vanishes. In fact, it can be shown that the ensemble of O_3 groups then form a structure belonging to the space-group T_h^6—$Pa3$, which should not exhibit optical activity. It is the small deviation from this arrangement that is responsible for the optical activity of both sodium chlorate and sodium bromate.

If the O_3 groups are taken to be isotropic, then clearly $B = 0$ and the right-hand side of equation (7) will be zero, so that $\rho = 0$. Thus, anisotropy of the individual groups is essential for optical activity to be present, as was mentioned in Part I.

We have calculated the anisotropy of the individual groups from theory in this paper. This is not quite necessary. In fact, they can be obtained from data on the scattering of light by solutions of the crystals. Studies of this type have been made for ions like SO_4 and NO_3 (Sweitzer, 1927), but not for ClO_3 or BrO_3 ions. If reliable experimental values are available for the anisotropy of the cations, then a more accurate comparison will be possible between theory and experiment.

SUMMARY

The theory of optical activity outlined in Part I has been applied to the cases of $NaClO_3$ and $NaBrO_3$. The calculated values for the rotatory power agree reasonably well with measurements previously reported.

REFERENCES

1. Bragg   .. *Proc. Roy. Soc.* 1924, **105A**, 370.
2. Dickinson and Goodhue   .. *J. Am. Chem. Soc.*, 1921, **43**, 2045.
3. Fajans and Joos   .. *Z. f. Phys.*, 1924, **23**, 1.
4. Kiby   .. *Ibid.*, 1923, **17**, 213.
5. Kolkmeijer, Bijeovet and Karsson   .. *Proc. Amst.*, 1921, **23**, 644.
6. Pauling   .. *Proc. Roy. Soc.*, 1927, **114A**, 191.
7. Rose   .. *Diss. Gött.*, 1909.
8. Sweitzer   .. *J. Phys. Chem.*, 1927, **31**, 1150.
9. Zachariasen   ,. *Z. Krist.*, 1929, **71**, 517,