

A REDETERMINATION OF THE ROTATORY DISPERSION OF SODIUM CHLORATE

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1. INTRODUCTION

SODIUM chlorate is the best known example of a crystal belonging to the cubic system exhibiting optical activity. As an aqueous solution of it does not display such activity, it is clear that the optical rotatory power is a consequence of the crystal structure which belongs to the space group T^h-P2_13 . Precise data regarding the rotatory power and its variation with wave-length are obviously needed as a starting point for any theoretical discussion of the optical behaviour of the crystal in relation to its structure. Determinations have been made in the visible region of the spectrum by Sohneke (1878), Voigt (1908), Perucca (1919) and also by Ramaseshan (1948). Measurements extending far into the ultra-violet were first made by Guye (1889) and later by Rose (1909), both of whom have obtained values of the rotation from 7200 A.U. to 2500 A.U. Though it is known that sodium chlorate transmits light upto nearly 2200 A.U., it appears that no one has since pursued the measurements farther into the ultra-violet. The data obtained by Guye and Rose, which are the most extensive, have been presented in Table I. From the data it can be seen that in the visible region Biot's Law is approximately valid, but as we proceed into the ultra-violet, the rotatory power increases at a much *slower* rate than is required by Biot's Law.

Though these experimental studies are on record, there appears to have been only one attempt to represent the data by means of a rotatory dispersion formula (Int. Crit. Tables, 1930). The formula is

$$\rho = \frac{1.078}{\lambda^2 - 0.0062} \quad (1)$$

But this formula is valid only from 7188 A.U. to 3184 A.U., and fails farther in the ultra-violet. This is to be expected since any one-term Drude equation varies faster with decrease of wave-length than expected from Biot's Law.

The present work was taken up with a view to redetermine the rotatory dispersion of sodium chlorate accurately and to extend the measurements

farther into the spectrum on either side. It has been possible to go up to 8756 A.U. in the infra-red and upto 2378 A.U. in the ultra-violet. Some significant results have emerged from these readings, which we shall describe later. A rotatory dispersion formula has been suggested which fits the data accurately over the whole range of wave-lengths. The relative merits of this formula and a formula of the Drude type have also been discussed.

Throughout, the rotatory power (ρ) is expressed in degrees per millimetre and λ in microns.

TABLE I
Rotatory Dispersion of Sodium Chlorate—Earlier Determinations

λ	ρ (Guye)	λ	ρ (Rose)
·2504	14·96	·2573	14·73
·2777	13·90	·2748	14·07
·2827	13·43		
·2992	12·42	·3256	10·67
·3234	10·79	·3404	9·80
·3337	10·08	·3467	9·44
·3564	8·861	·3611	8·69
·3735	8·100	·4308	6·01
·4071	6·754	·4862	4·67
·4283	6·055	·5270	3·94
·4553	5·331	·5893	3·13
·5310	3·881	·6563	2·50
·6507	2·559	·6867	2·27
·7177	2·068	·7188	2·07

2. EXPERIMENTAL DETAILS

Depending on the particular region of the spectrum which was being studied, four different experimental methods had to be employed. Before describing these in detail, we shall present the values of the rotatory power obtained by the various methods separately in Table II. The accuracy of the determinations by different methods have been checked against each other by arranging that they overlap, and as will be seen from Table II they agree satisfactorily.

We shall now describe the experimental procedure.

(A) A large crystal of sodium chlorate (about $5\frac{1}{2} \times 5 \times 4\frac{1}{2}$ cm.) grown in the Bell Telephone Laboratories* was used for these measurements. For

* The crystal was kindly loaned by Dr. R. S. Krishnan, to whom the author's thanks are due.

TABLE II
Rotatory Dispersion of Sodium Chlorate—Present Determination

λ	ρ				Most probable value of ρ
	A	B	C	D	
·23783				14·27	14·27
·23994				14·6	14·6
·24469			15·03		15·03
·246406			15·11	15·12	15·11
·24827		15·205	15·19		15·21
·2536		15·275	15·264		15·28
·25763		15·23		15·255	15·23
·2652		14·92			14·92
·26989		14·67			14·67
·27528		14·31			14·31
·28035		13·96			13·96
·28936		13·31			13·31
·29254		13·095			13·095
·29673		12·74			12·74
·30215		12·38			12·38
·31256		11·67			11·67
·33415		10·19			10·19
·36525	8·537	8·534			8·537
·37042		8·288			8·288
·39064		7·438			7·438
·40466	6·886				6·886
·40778	6·787				6·787
·43583	5·884				5·884
·49164	4·571	4·572			4·571
·54607	3·671				3·671
·57696	3·275				3·275
·57907	3·249				3·249
·5893	3·136				3·136
·62344	2·764				2·764
·69075	2·225				2·225
·7082	2·119				2·119
·77292	1·756				1·756
·8180	1·545				1·545
·8756	1·345				1·345

the visible and infra-red region of the spectrum, the polarimeter was of the simplest type consisting of two nicols. A high pressure mercury discharge lamp (Philips) served as a convenient multichromatic source of light from 9000 A.U. to 3650 A.U. By a suitable set of lenses parallel light was made to pass through the polarimeter and focus on the widened slit of a spectrograph. By taking photographs of the spectrum with different settings of

the analyser, the positions of extinction could be approximately determined for the different wave-lengths. To determine these readings more accurately, the photographs were repeated for much closer settings of the analyser on either side of extinction position for each wave-length. The time of exposure for these successive photographs was made exactly the same, varying from 30 seconds to 15 minutes depending on the brightness of the spectral line. By finding out the exposures of equal intensity on either side of the minimum, or in effect, by making use of the principle of the half-shade, the angle of extinction could be determined to within about 0.2° to 0.5° . By repeating these measurements with and without the crystal, the total rotation was estimated for the various wave-lengths. The thickness of the crystal was ascertained by means of a micrometer caliper measuring to an accuracy of 0.001 inch. A Hilger medium glass spectrograph was used for the visible spectrum. For the infra-red, a constant deviation instrument and special infra-red plates were employed. The photographs obtained in such a manner have not been reproduced here, but they exactly resemble the plates shown later. It can be seen that these plates look very much like the imprints of spectra obtained by Cotton and Descamps (see Lowry, 1935) with their polarimeter for measuring rotatory dispersion in the ultra-violet.

By replacing the entire glass optics in the above arrangement by corresponding quartz components, the measurements could just be extended upto 3650 A.U.

(B) Beyond 3650 A.U. in the ultra-violet, the absorption of light by the nicols became too great. Two natural crystals of calcite were used instead. When light is incident normally on one of the two parallel faces of calcite, the ordinary ray passes through undeviated, while the extraordinary ray, which is deflected, can be cut off by means of a suitable slit. One such crystal was mounted coaxially on a divided circle and served as the analyser while the other was fixed and was used as the polariser. A quartz mercury discharge lamp (Hanovia) was an excellent ultra-violet source of light. Though the aperture of this polarimeter was comparatively small, very satisfactory photographs were obtained as can be seen from Figs. 1, 2 and 3 in Plate XXII. The exposures in this region varied between 10 minutes and half an hour. In fact, calcite crystals have been used as polarisers by most of the pioneers working in this field (see Lowry, *loc. cit.*). In this manner, the rotation could be determined upto 2482 A.U., beyond which the absorption of light by the two calcite crystals began to creep in, so that even with exposures of 2 hours, the lines were too weak to be recorded.

(C) One of the calcite crystals was replaced by a reflection polariser as was used by Servant (1939) for the measurement of the rotatory dispersion of quartz in the Schumann region. A cleavage surface of a lithium fluoride crystal reflecting at Brewster's angle was found to give almost perfect polarisation. Transmission pictures revealed that the intensity of the light passing through the large specimen of sodium chlorate, which was being used for all the above measurements, was considerably cut off beyond 2446 A.U. It was therefore possible to measure the rotation only upto that wave-length by giving long exposures of half to one hour.

(D) But with thinner specimens of sodium chlorate the transmission extended easily upto 2300 A.U., without any notable diminution of intensity. To increase the transmitted light, the faces of the crystal were well polished by rubbing on a breathed-on glass surface. The readings were taken upto 2378 A.U., with a crystal of thickness 7.62 mm. by giving exposures of one hour.

The accuracy of the methods described above is quite high. For instance, the total rotation for 2536 A.U., for a thickness of 42.65 mm. is about 651.5° and this can be measured to within about 0.5° . If the thickness of the crystal is ascertained to an accuracy of 0.1%, the error in estimating the rotatory power is only about 0.2%. In this manner, the error of measurement for wave-lengths lying between 5893 A.U. and 2447 A.U. has been placed at 0.2 to 0.3%. As the total rotation is comparatively smaller farther in the ultra-violet (where the thin specimen of sodium chlorate was used) and in the infra-red region, the error is slightly greater, being a little over 1%. In the first three methods described above, the measurements were made at the room temperature, which was 25°C . approximately. But, when the readings were being taken with the thinner specimen (method D), the weather became rather humid and a heater had to be kept in the vicinity to prevent the crystal from getting damaged. Hence, the temperature rose to approximately 30°C .

3. DISCUSSION OF RESULTS

A comparison of Tables I and II shows that the general trend of the values obtained in the present determination agrees approximately with those of the earlier workers. In the visible region the agreement is extremely good. To illustrate this, the rotatory power as obtained by the various authors for a common wave-length is given in Table III.

In the ultra-violet, the present measurements give values slightly higher (about 1 to 2%) than those obtained by Guye and Rose. This might possibly

TABLE III

Name of Author	λ	ρ
Voigt590	3.170
Rose5893	3.13
Perucca5893	3.12
Ramaseshan5893	3.14
The present Author ..	.5893	3.136

be due to the difference in the temperature at which these measurements were made. Guye's values are given at 13° C. while the present data are at 25° C.

The small extension of the measurement into the ultra-violet has proved to be very fruitful. From the earlier measurements given in Table I, it will be seen that as we proceed into the ultra-violet the rate of increase of the rotatory power with decrease of wave-length becomes progressively smaller. This is also seen in the present determination but, in addition, it has been found that beyond 2536 A.U., there is an actual diminution in the magnitude of the rotation, the decrease becoming more pronounced as we move farther into the ultra-violet. This observation, which was first made with the large crystal of sodium chlorate, has been confirmed with the smaller specimen also. It appears that this anomalous behaviour of the rotatory dispersion of sodium chlorate has been noticed for the first time.

The photographs reproduced in Plate XXII were all obtained with the calcite polarising prisms (method B). In Fig. 1, the angle between each successive settings of the analyser is 8°. Though some lines have been over-exposed, the plate clearly shows the extinction positions for the different wave-lengths. As the specimen used was very large (42.65 mm.) four clear extinction bands are seen, the total rotation for the successive bands differing by 180°. Fig. 2 shows a similar photograph with much closer settings of the analyser (2°). Fig. 3 is an enlarged reproduction of the spectra obtained in the region of 2500 A.U. A line has been drawn through the minima of intensity for the different wave-lengths. It can be seen that extinction band changes its course beyond 2536 A.U., thus clearly demonstrating the diminution of the rotatory power in the ultra-violet. This observation has been verified with the smaller specimen also.

4. A ROTATORY DISPERSION FORMULA

As has already been pointed out, it is not possible to fit the data with a one-term formula of the Drude type. An attempt has therefore been made to represent the data by means of a two-term formula of the same type. The following formula gives an approximate fit:—

$$\rho = \frac{1.293}{\lambda^2 - (0.1)^2} - \frac{0.1724}{\lambda^2 - (0.21)^2} \quad (2)$$

This formula makes use of a characteristic wave-length at 1000 A.U., and another at 2100 A.U., almost at the limit of continuous absorption of light in sodium chlorate. The calculated and experimental values for a few wave-lengths are given in Table IV.

TABLE IV
Rotatory Dispersion using Formula (2)

λ	ρ (expt.)	ρ (calc.)
·2464	15.1	15.1
·2536	15.3	15.3
·2925	13.1	13.0
·3652	8.54	8.55
·5791	3.25	3.38

Though a fairly good fit has been obtained, the formula is questionable from the theoretical standpoint. For, it does not fulfil Kuhn's summation rule which states that the sum of the numerators determining the contributions of the different absorption frequencies to the rotatory power should vanish,

$$i.e., \text{ if } \rho = \sum_r \frac{Q_r}{\lambda^2 - \lambda_r^2}, \text{ then } \sum_r \frac{Q_r}{\lambda_r^2} = 0.$$

When this criterion is applied to (2), it is found that it is not even approximately satisfied, the strength of the positive term being nearly thirty times as great as that of the negative term. Hence it appears that a formula of the Drude type is not appropriate for the case of sodium chlorate. Instead,

TABLE V
Rotatory Dispersion using Formula (3)

λ	ρ (expt.)	Contribution of positive term	Contribution of negative terms	ρ (calc.)
·23783	14·27	29·831	15·697	14·13
·23994	14·6	29·134	14·637	14·5
·24469	15·03	27·673	12·629	15·04
·246406	15·11	27·165	12·011	15·15
·24827	15·21	26·637	11·393	15·24
·2536	15·28	25·208	9·884	15·32
·25763	15·23	24·211	8·947	15·26
·2652	14·92	22·495	7·536	14·96
·26989	14·67	21·529	6·835	14·69
·27528	14·31	20·493	6·153	14·34
·28035	13·96	19·59	5·61	13·98
·28936	13·31	18·533	4·818	13·32
·29254	13·10	17·659	4·582	13·08
·29673	12·74	17·06	4·30	12·76
·30215	12·38	16·338	3·974	12·36
·31256	11·67	15·075	3·455	11·62
·33415	10·19	12·897	2·682	10·22
·36525	8·537	10·524	1·986	8·538
·37042	8·288	10·195	1·901	8·294
·39064	7·438	9·052	1·619	7·433
·40466	6·886	8·371	1·464	6·907
·40778	6·787	8·231	1·433	6·798
·43583	5·884	7·115	1·199	5·916
·49164	4·571	5·487	0·895	4·592
·54607	3·671	4·389	0·711	3·678
·57696	3·275	3·909	0·636	3·273
·57907	3·249	3·880	0·632	3·248
·5893	3·136	3·740	0·610	3·130
·62344	2·764	3·324	0·548	2·776
·69075	2·225	2·687	0·457	2·230
·7082	2·119	2·552	0·439	2·113
·77292	1·756	2·131	0·382	1·749
·8180	1·545	1·896	0·351	1·545
·8756	1·345	1·650	0·320	1·330

the following formula has been suggested, which fits the newer measurements quite accurately over the entire range of wave-lengths:

$$\rho = \frac{1 \cdot 2387 \lambda^2}{[\lambda^2 - (0 \cdot 09)^2]^2} - \frac{0 \cdot 1374 \lambda^2}{[\lambda^2 - (0 \cdot 185)^2]^2} - 0 \cdot 123, \quad (3)$$

In this formula, the ultra-violet absorption wave-lengths are 900 A.U., and 1850 A.U. The third term represents the small contribution of the infra-red. As the exact behaviour of optically active crystals in the infra-red is not known, this contribution has been included in the form of a very small constant. The above formula is not open to the same objection as that raised against (2), for each term in (3), neglecting the infra-red, separately fulfils the summation condition, as has been shown in an earlier paper by the present author (1952). The calculated values are given in comparison with the experimental data in Table V. Though the weight of the negative term in formula (3) appears very small it can be seen from the table that contribution is very large in the ultra-violet, becoming almost equal in magnitude to that of the positive term.

It can be seen from the above table that the agreement is quite satisfactory, the deviation being generally within the limits of experimental error.

It can easily be shown that the characteristic wave-lengths occurring in rotatory dispersion formula (3) can also be used to represent the ordinary dispersion of sodium chlorate quite well. Accordingly, a formula of the Sellmeyer-Drude type involving these two wave-lengths has been fitted up. The formula is:—

$$n^2 - 1 = \frac{1.1825 \lambda^2}{\lambda^2 - (0.09)^2} + \frac{0.07992 \lambda^2}{\lambda^2 - (0.185)^2} - 0.00864 \lambda^2. \quad (4)$$

The third term represents a small infra-red contribution. The calculated values are given with the available experimental data. The values from

TABLE VI
The Dispersion of Sodium Chlorate

λ	n (expt.)	n (calc.)
·231	1·616	1·618
·2573	1·585	1·585
·2748	1·572	1·572
·3256	1·549	1·549
·3404	1·544	1·544
·3467	1·542	1·542
·3611	1·539	1·539
·4862	1·522	1·522
·5173	1·519	1·519
·5893	1·515	1·515
·6563	1·513	1·513
·6867	1·512	1·512
·7188	1·511	1·511

FIG. 1

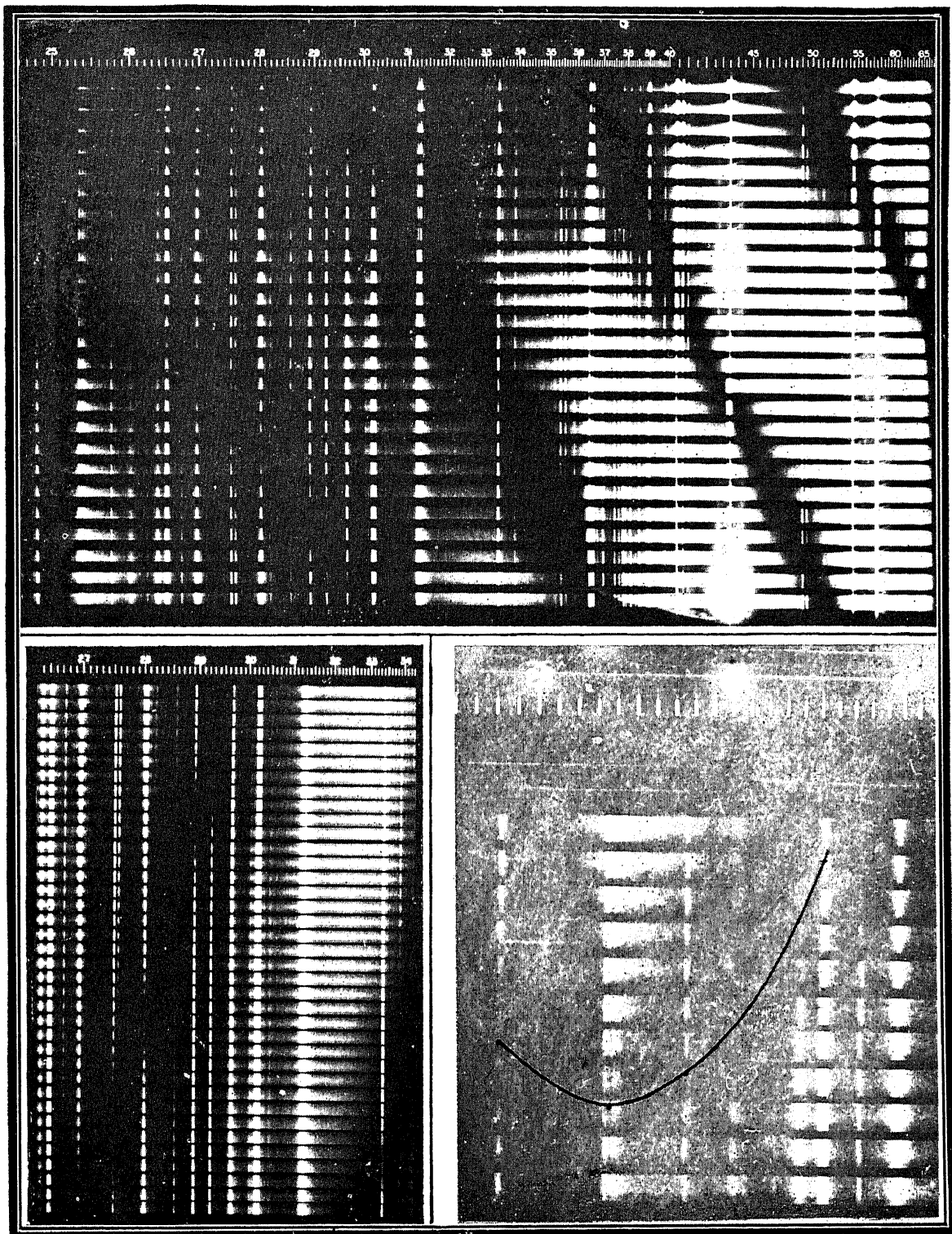


FIG. 2

FIG. 3

7188 A.U., to 2573 A.U., are from the data due to Rose (*loc. cit.*), while the value at 2310 A.U., is from Borel's determination (Landolt-Bornstein, 1923).

It can be seen that the calculated and experimental values agree very well. This indicates that the wave-lengths of 900 A.U. and 1850 A.U., appearing in formula (4), approximately represent the absorption wave-lengths of sodium chlorate.

In conclusion, I record here my thanks to Prof. Sir C. V. Raman for the encouragement and the suggestions he gave me during this work. My thanks are also due to Dr. S. Ramaseshan for the discussions I had with him.

5. SUMMARY

The rotatory dispersion of sodium chlorate has been redetermined and its wave-lengths range extended from 8756 A.U. to 2378 A.U. The rate of increase of the rotatory power with diminishing wave-length falls off in the ultra-violet. Beyond 2536 A.U. there is actually a diminution in the magnitude of the rotation, the value at 2378 A.U. being nearly 6% less than that at 2536 A.U. A rotatory dispersion formula of the Drude type containing a negative term gives a tolerable fit with the data, but such a formula is inappropriate since it violates the summation rule for optical rotatory power. The formula now proposed is

$$\rho = \frac{1 \cdot 2387 \lambda^2}{[\lambda^2 - (0 \cdot 09)^2]^2} - \frac{0 \cdot 1374 \lambda^2}{[\lambda^2 - (0 \cdot 185)^2]^2} - 0 \cdot 123.$$

It fits the data accurately over the whole range of wave-lengths, and is not open to the same objection. The negative term becomes comparable in magnitude to the positive term in the ultra-violet region. The characteristic wave-lengths appearing in the formula also fit the ordinary dispersion curve.

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