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Optical Rotatory Dispersion of Crystals of Sodium Chlorate and Sodium Bromate

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The rotatory dispersion of crystals of $NaClO_3$ and $NaBrO_3$ has been measured in the visible and ultraviolet region of the spectrum. Apart from a small infrared contribution, the rotatory dispersion of both crystals can be expressed as a difference of two terms. For $NaClO_3$ the positive term has a greater strength than the negative one, whereas for $NaBrO_3$ the reverse is the case. Thus corresponding configurations of the two crystals have opposite signs of optical rotation. The important point is brought out that calculations of optical activity in terms of atomic refractivities but neglecting rotatory dispersion, such as those carried out recently for these two crystals, are necessarily inconclusive.

Introduction

Bijvoet and his collaborators (Bijvoet, 1960; Beurskens-Kerssen, Kroon, Endeman, van Laar & Bijvoet, 1963) made the interesting discovery that crystals of $NaClO_3$ and $NaBrO_3$ with similar configurations have opposite signs of optical rotation. There have been attempts to calculate the rotatory powers of these crystals by means of the polarizability theory of optical activity. The first calculation, carried out by Ramachandran (1951), gave the correct sign of rotation for $NaClO_3$, as was verified later by the X-ray determination of its absolute configuration (Ramachandran & Chandrasekaran, 1957). In this calculation, Ramachandran substituted the oxygen atoms of each chlorate group by a single anisotropically polarizable particle and neglected the relatively small contributions of the sodium and chlorine atoms. It was naturally supposed that $NaBrO_3$ with a similar configuration would also have the same sign of rotation. That this was not so was proved by the X-ray work of Beurskens-Kerssen, Kroon, Endeman, van Laar & Bijvoet (1963), who then undertook a more detailed calculation treating each oxygen atom separately and found that the sign of rotation was extremely sensitive to the location of the oxygen. It appeared, therefore, that the reversal of sign in the case of the bromate could be accounted for satisfactorily by a small shift in the oxygen parameters within the limits involved.

However, it was emphasized by one of us (Chandrasekhar, 1963) that caution is necessary in using the polarizability theory for working out absolute configuration. The fundamental objection to the theory is that the influence of all the ultraviolet absorption bands is lumped into the polarizability of the atom and it is assumed that the bands contribute with the same relative strengths to the refraction and the rotation. But it is well known that strongly absorbing bands may be weakly optically active and *vice versa*, and that the rotational strengths of the bands may not all have the same signs. Bijvoet (1963) and Ramachandran (1963) have both expressed the view that this objection is not likely to affect the results of the optical calculations. The present investigation was taken up to test this important point.

Rotatory dispersion

We have determined the rotatory dispersion of $NaClO_3$ for 24 wavelengths from 0·2378–0·6234μ. The values agree to within 1% of those measured previously (Chandrasekhar, 1953*a*, 1961), but we place greater reliance on the new data because of improvements in the experimental arrangement. The set up was similar to that described recently by Kizel, Krasilov & Shamraev (1964). The rotatory dispersion is expressible by the formula

$$\varrho^{(+)}=\frac{1{\cdot}2374\lambda^2}{[\lambda^2-(0{\cdot}09)^2]^2}-\frac{0{\cdot}1355\lambda^2}{[\lambda^2-(0{\cdot}185)^2]^2}-0{\cdot}123\,, \qquad (1)$$

with a positive term at 0·09μ, a negative term at 0·185μ and a third term representing a very small negative infrared contribution (ϱ is throughout expressed in deg.mm^{-1} and λ in μ). The r.m.s. deviation between the calculated and experimental values is 0·03 deg.mm^{-1} and the maximum deviation 0·65%. We shall suppose that the crystal has *positive* rotation and configuration *A*.

We have made similar measurements of the rotatory dispersion of $NaBrO_3$ for 19 wavelengths from 0·2752 to 0·6234μ. For a crystal of similar configuration (configuration *A*), the rotatory dispersion can be represented by

$$\varrho^{(-)}=\frac{0{\cdot}6095\lambda^2}{[\lambda^2-(0{\cdot}09)^2]^2}-\frac{1{\cdot}0459\lambda^2}{[\lambda^2-(0{\cdot}2)^2]^2}-0{\cdot}093\,, \qquad (2)$$

with r.m.s. deviation 0·05 deg.mm^{-1} and maximum deviation 0·51%. The position of the negative term in this formula is only slightly different from that for $NaClO_3$, but its strength is now greater than that of the positive term. Thus the rotatory power of $NaBrO_3$ is *negative* for configuration *A*.

The refractive dispersion of $NaClO_3$ in the range 0·231–0·7188μ has been shown to be expressible by the formula

$$n^2-1=\frac{1\cdot1825\lambda^2}{\lambda^2-(0\cdot09)^2}+\frac{0\cdot07992\lambda^2}{\lambda^2-(0\cdot185)^2}-0\cdot00864\lambda^2\,, \quad (3)$$

which has the same characteristic wavelengths in the ultraviolet as (1) (Chandrasekhar, 1961). The corresponding formula for $NaBrO_3$, using the characteristic wavelengths of (2), is

$$n^2-1=\frac{1\cdot3194\lambda^2}{\lambda^2-(0\cdot09)^2}+\frac{0\cdot2357\lambda^2}{\lambda^2-(0\cdot2)^2}-0\cdot0174\lambda^2\,, \quad (4)$$

to which agrees with the data extending from 0·2967 0·7682μ due to Poinsot & Mathieu (1955); the r.m.s. deviation between the calculated and experimental values of n is 4×10^{-4} and the maximum deviation 9×10^{-4}.

The relationships between $|\varrho|$ and λ for the two crystals are shown in Fig. 1. Apart from the very small infrared contribution (1) and (2) are of the quadratic type, first proposed for α-quartz and cinnabar (Chandrasekhar, 1952, 1953*b*, 1961). Subsequently there have been a number of investigations on the applicability of this formula to crystals. Kizel, Krasilov & Shamraev (1964) found that the formula holds good for β-quartz and ethylenediamine sulphate. Agranovich (1957) showed that the quantum theory of crystalline optical activity leads to the expression

$$\varrho=\sum_i\frac{K_i^{(1)}\lambda^2}{(\lambda^2-\lambda_i^2)^2}+\sum_i\frac{K_i^{(2)}(\lambda^2+\lambda_i^2)}{(\lambda^2-\lambda_i^2)^2}\,, \quad (5)$$

which, in fact, reduces to the quadratic formula when $\lambda\gg\lambda_i$. Formula (5) fits the rotatory dispersion of some crystals of salts of dithionic acid (Beljaev & Perekalina, 1966). Nevertheless it would be fair to say that the precise nature of the rotatory dispersion term has been established unequivocally in only two crystals, *viz.* benzil (Kizel, Krasilov & Shamraev, 1964) and sodium uranyl acetate (Kizel, Krasilov & Shamraev, 1965), for which measurements through an absorption band have proved the validity of the Drude term near the band. It should be noted, however, that there is an important difference between benzil and sodium uranyl acetate on the one hand and crystals such as quartz, cinnabar, sodium chlorate and sodium bromate on the other. X-ray analysis has shown that the molecules of benzil (Brown & Sadanaga, 1965) and sodium uranyl acetate (Zachariasen & Plettinger, 1959) possess neither a centre nor a plane of symmetry in the crystal structure. Thus, although these substances are optically inactive in solution, their activity in the crystalline state will be partly of molecular origin and some rotatory dispersion terms may indeed be expected to be of the Drude type.

When this investigation was in progress, Kizel, Krasilov & Shamraev (1964) carried out measurements on $NaBrO_3$ and published a Drude type of formula, which, for configuration A, may be written as

$$\varrho^{(-)}=\frac{1\cdot449}{\lambda^2-(0\cdot1)^2}-\frac{1\cdot887}{\lambda^2-(0\cdot224)^2}\,. \quad (6)$$

The formula agrees with our experimental values to within about 2%. It has been shown that the rotatory dispersion of $NaClO_3$ may also be expressed approximately by a similar Drude type formula (Chandrasekhar, 1953*a*, 1961). On the basis of the new experimental data we have modified it to

$$\varrho^{(+)}=\frac{1\cdot2528}{\lambda^2-(0\cdot1)^2}-\frac{0\cdot1546}{\lambda^2-(0\cdot21)^2}\,, \quad (7)$$

again for configuration A. The formula fits all the observed values to within 2·2% except that for 0·62344μ for which the discrepancy is 2·9%. Though (1) and (2) give a much better fit with experiment than (7) and (6) respectively, it is not possible at this stage to assert which type of formula is valid for $NaClO_3$ and $NaBrO_3$ (see Chandrasekhar, 1961).

Conclusion

Whether we consider the Drude or the quadratic equation, the formulae for $NaClO_3$ and $NaBrO_3$ can be seen to be quite similar. The essential difference between the two is that in the former the contribution of the positive term is greater than the negative one, whereas in the latter the reverse is the case. Thus corresponding configurations of the two crystals have opposite rotatory powers. On the other hand, the terms are all positive in refractive dispersion. Consequently a theory which seeks to calculate optical activity in terms of atomic refractivities, but without taking into account rotatory dispersion, is necessarily incomplete and liable to give ambiguous results.

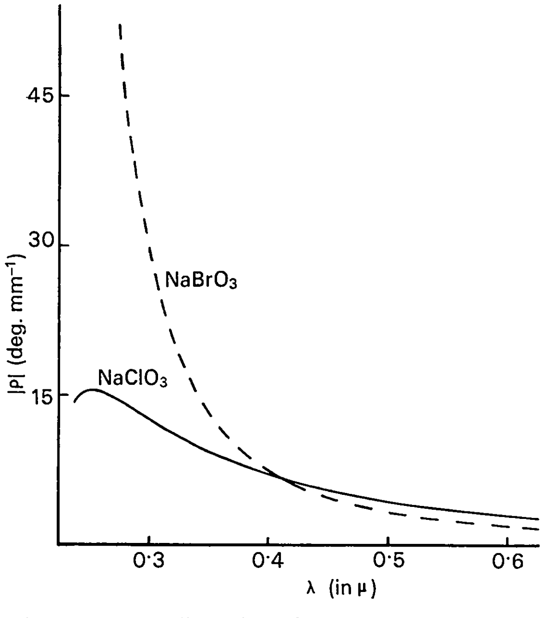

Fig. 1. Rotatory dispersion of $NaClO_3$ and $NaBrO_3$.

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Geometrical Symbols for All Crystallographic Symmetry Groups up to Three Dimensions

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A complete list of the individual symmetry groups belonging to all sets of such groups up to three dimensions is given, each set being characterized by symbols as agreed upon by the Commission on *International Tables* and each symmetry group by a symbol closely connected with the international space group symbols. Each set is characterized by the reducibility of the matrices of the transformations of space corresponding to the symmetry operations.

As pointed out elsewhere (Bohm & Dornberger-Schiff, 1966) the different kinds of symmetry group – not only the purely geometrical groups but also those including antisymmetry and other generalized symmetry – may be described and symbolized as geometrical symmetry groups. It is of advantage to have easily understandable symbols for the different sets of symmetry groups – differing *e.g.* in their dimensions of extension or periodicity – and also for the individual symmetry groups of these sets.

In the following a complete list of the symmetry groups of all sets up to three dimensions is given. In Tables 1 and 2 symbols for these sets are used (symbols $\mathscr{G}$) as agreed upon by the Commission on *International Tables* and originally proposed by Niggli (1966). For comparison, symbols for the sets proposed some time ago by one of the present authors (Bohm, 1963) are given (symbols *G*).

Because we included the possibility that one or more dimensions have a non-geometrical meaning, subsets of symmetry groups are of importance in which some of the directions (although all with or all without periodicity) are not exchanged by the transformations of the groups. This is indicated in the symbol of the subset by enumerating separately the dimensions which do not exchange (see below).

The matrices representing the symmetry groups of such a set are at least reducible in a characteristic way indicated in the line below the *G*-symbols. Matrices with 4 or 3 rows respectively are used in which the last column gives the translational components.

All symbols for the symmetry groups are deduced from the (full) international space group symbols in the following way: The symbols for the symmetry elements retain their well-known meaning. Symmetry elements referred to directions of missing periodicity are enclosed in round brackets. If two or more such directions of missing periodicity exist, and if exchange of these directions is possible within the particular set, the corresponding symmetry symbols are enclosed in