

THE OPTICAL ROTATORY DISPERSION OF CINNABAR

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1. INTRODUCTION

CINNABAR is the bright red crystalline form of mercuric sulphide which occurs as hexagonal prisms or plates belonging to the space group D_3^4 (or the enantiomorphous D_3^6). The crystal exhibits a very marked optical rotatory power. This has been measured for a direction coinciding with the optical axis by several workers, notably by Becquerel (1908), Rose (1910) and Molby (1910). At room temperature, measurements have been made only upto the yellow line of sodium, since in these circumstances the crystal is almost completely opaque beyond that wavelength. But at liquid-air temperature, the measurements have been extended farther into the shorter wavelength region, for at such a low temperature, even a specimen as thick as 1.5 mm. transmits light upto 5600 A.U. The values obtained by the different authors do not agree very well, probably due to the variations in the quality of the specimens employed. But even so, it is clear that the rotatory power of cinnabar is extremely large and also that it varies considerably with the wavelength, the value increasing by about four times as we proceed from 7200 to 6000 A.U. Another fact which emerges from the observations of Becquerel and Molby is that the rotation increases notably when the temperature of the crystal is raised. As far as can be judged from the present data, the rate of variation of the rotatory power with temperature increases with decrease of wavelength at a much faster rate than does the rotatory power itself.

In the present paper, it is proposed to consider the variation of the rotatory power with wavelength as also with temperature. It is shown that a Drude equation does not fit the rotatory dispersion satisfactorily, whereas a formula of the type

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2} \quad (1)$$

represents it much better. By assuming that the characteristic absorption wavelength λ_0 shifts with temperature, it has been possible to quantitatively account for the temperature coefficient of the rotatory power.

2. THE ROTATORY DISPERSION FORMULA

Rose (*loc. cit.*) has attempted to fit his experimental data by means of a rotatory dispersion formula similar to that suggested by Drude for quartz (1900), but with both terms having the same sign. The formula proposed by him is

$$\rho = \frac{21 \cdot 8835}{\lambda^2 - 0 \cdot 31821} + \frac{1 \cdot 6361}{\lambda^2} \quad (2)$$

The first term which accounts for the bulk of the rotation makes use of an absorption at about 5640 A.U., while the second term represents the small contribution due to a characteristic frequency lying in the extreme ultra-violet. The values calculated from this formula are given with the experimental data of Rose in Table I. Throughout ρ is expressed in degrees per millimetre and λ in microns.

TABLE I

λ	$\rho_{(\text{expt.})}$	$\rho_{(\text{calc.})}$	$\rho_{\text{calc.}} - \rho_{\text{expt.}}$
·5983	554·98	554·96	- 0·02
·6022	489·64	497·05	+ 7·41
·6103	417·00	407·77	- 9·23
·6136	396·44	379·65	-16·79
·6192	365·37	339·91	-25·46
·6247	337·42	307·97	-29·45
·6278	322·50	292·40	-30·10
·6337	303·43	266·59	-36·84
·6495	255·60	215·59	-40·57
·6563	241·40	198·29	-43·11
·6870	182·00	145·79	-31·21
·7187	132·57	113·51	-19·06
·7621	86·16	86·16	0·00

It can be seen that the experimental values differ from those calculated in a systematic fashion, the deviation being throughout rather large and negative. Apart from this, there is another objection to the formula proposed, namely, that it assumes the existence of a characteristic absorption wavelength at 5640 A.U., while actually, according to the observations of Becquerel,

cinnabar is capable of transmitting light upto 5600 A.U. at liquid-air temperature, and at that temperature the rotatory power for that wavelength is only about 1.75 times larger than that for 6000 A.U. and of the same sign. These facts indicate *prima facie* that the characteristic absorption band lies farther out towards the blue end of the spectrum, though, of course, both its position and width may be expected to be temperature-sensitive.

In an earlier paper (1953), the present author had given a theoretical interpretation of the optical activity of quartz, in which the expression for the rotatory power had been derived to be of the same general type as (1). We shall see whether the same theory may be applied to the case of cinnabar. The structure of cinnabar is similar to that of quartz, both crystals belonging to the space group D_3^4 or D_3^6 . Also, just as for quartz, the optical activity of cinnabar is purely a consequence of its crystal structure. Obviously then, whatever arguments hold good for quartz should be applicable to the case of cinnabar and hence its rotatory power should be capable of being fitted by a similar formula. In fact, the following formula is found to represent it well, as can be seen from Table II.

$$\rho = \frac{19.13 \lambda^2}{(\lambda^2 - 0.243)^2} \quad (3)$$

TABLE II

λ	$\rho_{\text{(expt.)}}$	$\rho_{\text{(calc.)}}$	$\rho_{\text{calc.}} - \rho_{\text{expt.}}$
.5983	555	518	- 37.0
.6022	489.6	484.6	- 5.0
.6103	417.0	425.1	+ 8.1
.6136	396.4	404.0	+ 7.6
.6192	365.4	372.0	+ 6.6
.6247	337.4	344.3	+ 6.9
.6278	322.5	330.1	+ 7.6
.6337	303.4	305.5	+ 2.1
.6495	255.6	255.1	- 0.5
.6563	241.4	233.8	- 7.6
.6870	182.0	172.2	- 9.8
.7187	132.6	132.0	- 0.6
.7621	86.2	97.4	+11.2

The formula makes use of an absorption at 4930 A.U. which is well within the limit of continuous absorption of light and therefore, is certainly more reasonable than the wavelength occurring in (2).

It can be seen that the fit is throughout good except for λ 5983 A.U. and λ 7621 A.U. But even this discrepancy is not of any significance. For, the uncertainty of the measurement of the rotatory power has been found by Rose to be much larger for these two wavelengths than for the others. Also it will be noticed that the difference between the calculated and experimental values is not of a progressive nature, being sometimes positive, sometimes negative.

It can easily be shown that the characteristic wavelength appearing in (3) can also fit the ordinary dispersion curve fairly well. Accordingly, a formula of the Sellmeyer-Drude type involving this wavelength has been fitted up for the ordinary index. It is found that the bulk of the refraction is due to an extreme ultraviolet term whose contribution has been replaced by a constant. The formula is

$$n^2 - 1 = 5.7 + \frac{0.5594 \lambda^2}{\lambda^2 - 0.243} \quad (4)$$

The calculated and experimental values are given in Table III. The data were obtained from the *International Critical Tables* (1930).

TABLE III

λ	$n_{(\text{expt.})}$	$n_{(\text{calc.})}$
.599	2.903	2.904
.6075	2.887	2.887
.6239	2.865	2.863
.6439	2.842	2.838
.6720	2.816	2.813
.7077	2.789	2.790
.7621	2.760	2.768

It will be seen that the agreement is tolerably good, thus indicating that the characteristic wavelength at 4930 A.U. approximately represents the actual dispersion wavelength of cinnabar.

3. THE TEMPERATURE VARIATION OF THE ROTATORY POWER

We shall now discuss the influence of temperature on the optical rotatory power. In an earlier paper (1952), the present author had quantitatively

accounted for the temperature coefficient of the rotatory power of quartz over a wide region of the spectrum by assuming that the characteristic frequency shifts with temperature. We shall now apply the same method to the case of cinnabar. As was done for quartz, we shall neglect all considerations of thermal expansion in these calculations as its contribution to the temperature coefficient is comparatively small. The rotatory dispersion formula (1) may be expressed in the form

$$\rho = \frac{a\nu^2}{(\nu_0^2 - \nu^2)^2}, \quad (5)$$

where $\nu = 1/\lambda$ and $k = a\lambda_0^4$. Differentiating with respect to temperature, we get

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{4 a\nu^2\nu_0^2}{(\nu_0^2 - \nu^2)^3} \chi_0 \\ &= \frac{4 k\lambda^4}{(\lambda^2 - \lambda_0^2)^3} \chi_0, \end{aligned} \quad (6)$$

where
$$\chi_0 = -\frac{1}{\nu_0} \frac{d\nu_0}{dt} = \frac{1}{\lambda_0} \frac{d\lambda_0}{dt}.$$

Molby has made measurements of the rotatory power at room and liquid-air temperatures for a few wavelengths. Using these data, the rate of increase of the rotatory power with temperature has been estimated for two wavelengths. Substituting for K and λ_0 in (6) and putting $\chi = 7.0 \times 10^{-5}$, $d\rho/dt$ has been theoretically calculated for these wavelengths. These are given in Table IV along with the experimental values.

TABLE IV

λ	$d\rho/dt$ (expt.) (-186° to 20° C.)	$d\rho/dt$ (calc.) $\chi = 7 \times 10^{-5}$
·5893	..	0·57
·6438	0·18	0·18
·6708	0·12	0·12

Molby has also measured the rotatory power for the red line λ 6438 A.U. at various temperatures ranging from -188° C. to 20° C. in steps of about 15° C. It is found that the positive temperature coefficient becomes progressively smaller as the temperature of the crystal is lowered.

Proceeding in the same manner as before, χ has been calculated for the different temperatures. The values are given in Table V.

TABLE V

Temp. °C.	dp/dt	$\chi \times 10^5$
+12.3	0.26	9.9
- 6.5	0.27	10.5
- 32	0.24	9.1
- 55	0.17	6.4
- 79	0.23	8.8
- 98	0.29	11.0
-112	0.19	7.2
-136	0.08	3.2
-155	0.03	1.0
-167	0.05	1.9
-180	0.09	3.4

Because of the difficulty of measurement there are some spurious fluctuations in the experimental values of dp/dt , but broadly speaking, one can see that χ tends to become very small at the lower temperatures. In fact, many crystals exhibit a similar behaviour, the rate of shift of their characteristic frequencies, as estimated from the thermal variation of the refraction, being found to diminish to negligible values at very low temperatures.

It would be of interest to see how the value of χ calculated above compares with that obtained from the thermal variation of the refractive indices of cinnabar. Values of dn/dt for both the indices are given in the *International Critical Tables* (1930) for a few wavelengths. With these data and the formula (4), χ has been evaluated for the ordinary index in the manner suggested by Ramachandran (1947). It has been assumed that the extreme ultraviolet absorption does not shift with temperature. We then get the expression

$$\frac{dn}{dt} = -\frac{\gamma(n^2 - 1)}{2n} + \frac{1}{n} \frac{k\lambda^4}{(\lambda^2 - \lambda_0^2)^2} \chi_0,$$

where γ is the coefficient of cubical expansion, $k = 0.5594$ from (4) and χ_0 and λ_0 have the same significance as before. The value of γ has been estimated from the linear expansion data (*International Critical Tables*) and is found to be equal to 57.3×10^{-6} . Putting $\chi = 10.5 \times 10^{-5}$, dn/dt has been calculated for a few wavelengths and has been presented in Table VI.

TABLE VI

λ	$\frac{dn}{dt} \times 10^5$ (expt.) (-50° to +12° C.)	$\frac{dn}{dt} \times 10^5$ (calc.) $\chi = 10.5 \times 10^{-5}$
.599	13	12
.6075	9	10
.624	8	7
.644	5	5
.718	2	1

The agreement between calculated and experimental values is quite good. It will be seen that the values of χ as estimated from the temperature coefficients of rotation and refraction are about the same. It should be remarked that the data of $d\rho/dt$ appearing in Table IV are the values at a temperature of about -80° , while those of dn/dt in Table VI are given at -20° C. Hence χ is slightly less in the former case.

In conclusion, I express my best thanks to Prof. Sir C. V. Raman for the useful discussions I had with him during the course of this work.

4. SUMMARY

It is shown that a rotatory dispersion formula of the Drude type is inappropriate in the case of cinnabar. On the other hand, a formula of the type $\rho = k\lambda^2/(\lambda^2 - \lambda_0^2)^2$, which has been arrived at from certain theoretical considerations, represents it well. The characteristic wavelength used in this formula also fits the ordinary dispersion curve. By assuming that λ_0 shifts with temperature, the thermal coefficient of the rotatory power has been quantitatively accounted for, the rate of change of λ_0 being found to be about the same value as that estimated from the thermal variation of refraction.

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