7th April 1930

The Pleochroism of the Nitrate Ion in the near Ultra-Violet.

Light from a quartz mercury lamp was passed through a ~~quartz~~ Glan ultra-violet polariser* and was then incident on crystals of sodium or potassium nitrate attached by a trace of wax at one extreme end of the crystal to a parallel plate of fused quartz. The transmitted light was then spectrographed with a Hilger quartz instrument, the slit which was wide open, being placed just behind the crystal specimen.

1. $NaNO_3$ crystal was attached with one of the faces of the rhomb ~~[illegible]~~ touching the quartz plate, and normal to the path of the light,

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* Halle's, borrowed from Dr J. C. Ghosh. – Square-ended, with air gap between the component prism

the short diagonal of the rhombus being horizontal. The transmitted light was spectrographed both when the axis of transmission of the polariser was vertical and also when it was horizontal. In both cases there is an appreciable absorption whose maximum lies somewhere about 3000 A.U. and extends considerably on either side; but the absorption was much greater when the incident vibration was vertical than when it was horizontal.

2. The crystal of $NaNO_3$ was turned in its own plane ($\perp^r$ to direction of incid. light) so as to make the short diagonal now vertical. The absorption is now much greater when the incident vibration is hori-

zontal than when it is vertical.

So in either case the absorption is greater when the incident vibration is $\perp^r$ to the shorter diagonal of the face.

KNO_3

1. The crystal was set with its "c" axis vertical and its "b" axis along the direction of the light. i.e. the light traversed the "ac" planes (which are natural faces) of the crystal.

When the incident vibration is vertical i.e. along the "c" axis, there is very little absorption. On the other hand when the incident vibration is horizontal, the absorption is considerable.

2.) The crystal was rotated about the "b" axis, so as to make the "c" axis horizontal and the "a" axis vertical.

The absorption is now considerable when the incident vibration is vertical and is very small when the incident vibration is horizontal.

The results with both the nitrates can be interpreted thus:-

The λ 3000 absorption is practically nothing when the incident vibration is perpendicular to the plane of the nitrate ions in the crystals, but is very large when the incident vibrations are in the plane of the NO_3 ions; i.e. the particular absorption frequency corresponds to vibrations in the plane of the NO_3^- ion.

A critical examination of the absorption pictures shows that for the component in the plane of the NO_3^- ion the absorption begins with the 3132-26 doublet of the Hg arc; all the lines between this doublet and the 2803 line are more or less completely absorbed: 2803 itself is just transmitted, the transmission increasing afterwards up to about 2640 when it reaches a maximum and (for shorter wavelengths) again ~~begins~~ ~~another~~ the absorbtion increases. On the other hand ~~for~~ (the transmission of) the $\perp^r$ component is practically constant up to the 2537 line, where the absorption begins.

R. A. Morton and R. W. Riding (Proc. R.S., A, 113, 717, (1927)) have investigated the absorption spectra of 8 nitrates in solution in water (at different concentrations) and obtain an absorption whose maximum is at about 3000 A.U and whose min. is at about 2630 A.U., with slight variations from substance to substance and also with concentration.

According to these authors in addition to the above selective absorption, there is also a general absorption which is practically zero at 3000 A.U. and rises gradually as we proceed towards the ultra violet.

G. Scheibe, R. Römer and G.

Rossler (Ber. d. Chem. Ges., 59, 1321, (1926)) obtain another absorption band for NaNO_3 (which they have investigated ~~in for~~ shorter wave-lengths) at λ 1940, almost at the limit of their range of investigation. In fact there is only one point in their curve of absorption on the shorter wave-length side of the above absorption maximum; and it can not therefore be inferred with any definiteness from their curves whether the absorption will fall down appreciably as we proceed further on the shorter wave-length side. [See however p. 51]

Konr. Schaefer (Zeit. anorg. Chemie, 97, 285 (1916)) has investigated some nitrates both organic and inorganic (including HNO_3) and finds an absorption band at 3350 wave-numbers per mm., i.e. at λ 3000. For molten KNO_3 he gets a broad band from wave numbers 3140 to 3500 mm^{-1}. i.e. in about the same position.

K. Schaefer (Zeits. f. wiss. Photogr., 8, 260 (1910)) has also investigated the absorption by KNO_3 solid and records an absorption in the same region of the spectrum. He has not investigated the directional properties, however.

8th Apr. 1930

Refractive indices of $NaNO_3$ and KNO_3 crystals (from Groth)

$NaNO_3$. (Schrauf) $\frac{M}{\rho} = 37.45$

	λ	ω	ε	ω − ε
B	6867.5	1.5793 (12.46)	1.3346 (7.75)	·2447 (4.71)
C = 6563.0				
D	5893	1.5874 (12.59)	1.3361 (7.77)	·2513 (4.82)
E	5269.7	1.5954 (12.73)	1.3374 (7.79)	·2580 (4.94)
H	3968.6	1.6260 (13.25)	1.3440 (7.93)	·2820 (5.32)

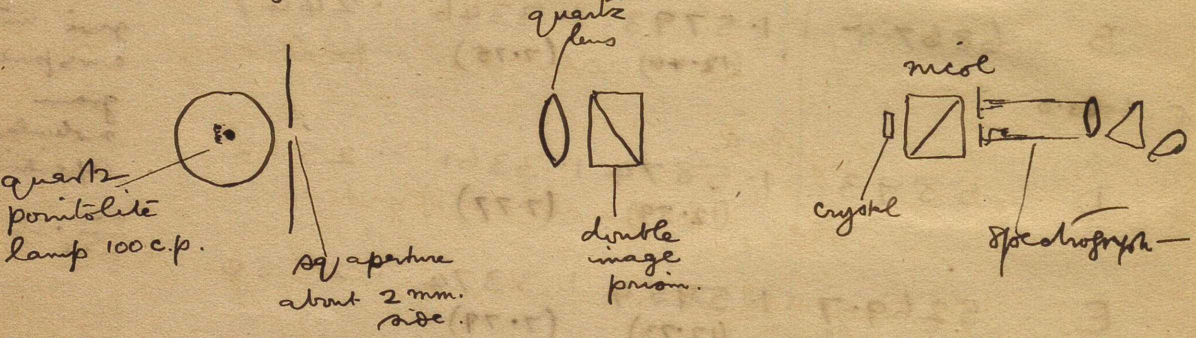
The numbers inside the brackets give the corresponding gram molecular refractivities $\frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho}$.

KNO_3 (Schrauf) $\frac{M}{\rho} = 47.85$

λ	α	β	γ	$\frac{\beta+\gamma}{2} - \alpha$
B	1.3328 (9.85)	1.4988 (14.05)	1.4994 (14.05)	·1663
D	1.3346 (9.90)	1.5056 (14.22)	1.5064 (14.22)	·1714
E	1.3365 (9.95)	1.5124 (14.36)	1.5135 (14.41)	·1765
H	1.3436 (10.14)	1.5385 (14.99)	1.5405 (15.03)	·1959

23rd Apr. 1930

A thin crystal of KNO_3 with two of its "ac" faces (010) well developed was selected and mounted between two crossed nicols, and the transmitted light was spectrographed. The actual arrangement was as below:



The quartz lens was first adjusted to focus the aperture on the spectroscope slit and the double image prism placed ~~at~~ sufficiently ~~dist. from~~ close to the lens to separate clearly the two images of the aperture falling on the slit of the spectroscope. The crystal was adjusted to have the ac plane $\perp^r$ to the direction of light, in the path one of the doubly refracted beams emerging from the double image prism. Its "c" axis was at about 45° to the axis of separation of the ~~[illegible]~~ two images. The quartz nicol was placed immediately behind the crystal and rotated so as to quench completely the vibration falling on the crystal.

The interference system was then photographed, taking alongside it a Hg comparison spectrum. The following were the measurements on the plate

λ in A.U.	6868 B	5893 D	5270 E	4358 of Hg.	3969 H	3663.
no. of fringes	1·3	30·9	57·4	116·0	154·4	194·3

The numbers refer to an arbitrary zero. Integral values correspond to maximum brightness (the fringes were measured at the centre of the dark lines in the negative) and excepting for an additive integral constant determined by the zero of the arbitrary scale ~~is given co~~ corresponds to the n of the following relation

$$(\mu_1 - \mu_2)\,t = (2n+1)\,\frac{\lambda}{2}$$

where t is the thickness of the crystal and μ_1 and μ_2 are the two principal refractive indices in the ac plane of the crystal i.e. α and β.

The thickness could not be measured accurately since the ~~crystal~~ sides of the crystal were not perfectly plane throughout, being of the form . However rough measurements gave for the upper limit of the thickness 0.64 mm.

It was therefore considered desirable in determining the values of β − α in the ultra violet for the crystal to assume two values for β − α from the measurements of Schrauf in the visible region and to eliminate t. Since any slight deviation from normality to the path of the light, of the faces of the crystal will in effect be equivalent to a small change in the thickness of the crystal, this method of eliminating t avoids also ~~at~~ automatically the effects of small errors in the setting of the crystal.

Assuming Schrauf's values for $\beta - \alpha$ for the B and H lines, viz 0·1660 and 0·1949 respectively the effective thickness t of the plate comes out as

$$\underline{t = 0{\cdot}614 \text{ mm}}.$$

as against the upper limit of 0·64 obtained with the spherometer.

Using this value of the thickness, the value of n comes out as the value on the arbitrary scale **plus** 147. The values of $\beta - \alpha$ are calculated for other wave-lengths and given in the following table.

λ A.U.	no. on the arbitrary scale	n = no. on previous column + 147	$\beta - \alpha$ for KNO_3 Calculated	Schrauf's
6868 (B)	1·3	148·3	(·1664)	·1660
5893 (D)	30·9	177·9	·1712	·1710
5270 (E)	57·4	204·4	·1759	·1759
4358	116·0	263·0	·1870	—
3969 (H)	154·4	301·4	(·1952)	·1949
3663	194·3	341·3	·2039	—

24th Apr

The results of the measurements on another photographic plate taken with the same crystal at a different time are given in the following table. The values of $\beta-\alpha$ for the E and H lines were assumed and the thickness of the crystal came out as

$$t = 0\cdot 616 \text{ mm.}$$

in good agreement with the previous value. The calculated values of $\beta-\alpha$ for different wavelengths are as below.

	λ	no. of fringe arbitrary	$n = n_{arb.} + 203$	$\beta-\alpha$ calcd.	Schrauf's
E	5270	1·7	204·7	(·1756)	·1759
#	4358	60·1	263·1	·1869	—
H	3969	98·6	301·6	(·1946)	·1949
	3663	138·6	341·6	·2039	—
last fringe that could be measured	3376	190·0	393·0	·2157	—

The rapid increase of the ordinary ref. index with diminishing wave-length as contrasted with the slow increase of the extraordinary index is in agreement with our observation regarding the polarisation of the near ultra violet ~~band~~ frequencies of the NO_3 ion.

In this connection it is interesting to note that F. F. Martens (Ann. der Physik, (4) 6, 603 (1901)) in his table of refractive indices for $CaCO_3$ (~~which~~ CO_3 has a structure quite similar to the NO_3 ion) gives for his shortest wavelength viz Al. ·198 μ a value for the extraordinary ray while ~~for~~ the column for the ordinary ray is left blank. In ~~his~~ recently editing the data on ref. indices of crystals for Landolt Bornstein Tables (5th ed., 1923) remarks that due to absorption it is not possible to measure beyond ·199 μ. It is clear that the absorption begins first for the ordinary ray.

Also the ordinary ref. index shows at about 2000 A.U. very rapid increase with diminishing wave-length, while the extraord. index increases slowly as we should expect. In fact by using a dispersion formula of the type

$$n_\omega^2 = m_o + \frac{m'_\omega \lambda^2}{\lambda^2 - {\lambda'_\omega}^2} + \frac{m''_\omega \lambda^2}{\lambda^2 - {\lambda''_\omega}^2}$$

he gets for the ~~ex~~ ordinary vibration two natural frequencies at

$$\lambda'_\omega = \cdot 100\,\mu \text{ and } \lambda''_\omega = \cdot 160\,\mu$$

while for the ~~e~~ extraordinary ray

a single frequency is sufficient

$$n^2 = m_\varepsilon + \frac{m'_\varepsilon \lambda^2}{\lambda^2 - \lambda'^2_\varepsilon}$$

where $\lambda' = \cdot 106\ \mu$

Thus the frequency at $\cdot 160\ \mu$ is polarised, existing only for vibrations in the plane of the CO_3 group while the frequency at about $\cdot 100\ \mu$ is common to both ~~and~~ ie is unpolarised. Probably it is the natural frequency of the Ca ion which is practically isotropic

26th Apr. 30

~~In~~ The well known Lorentz expressn. for refractivity

$$R = \frac{n^2-1}{n^2+2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N A$$

where A is the moment induced in each refracting particle ~~molecule~~ and N is the no. of such particles in a mass M of the ~~medium~~, is based on the assumption that the influence of the doublets inside the Lorentz sphere is equal to zero; which is true only for an isotropic crystal. According to Bragg in a crystal like $CaCO_3$ or $NaNO_3$, we have to take the mutual influence ~~als~~ of the neighbouring atoms also into account. If we take any CO_3 or NO_3 group by far the greatest contribution ~~comes~~ to the refractivity comes from the three O^{--} ions; and in calculating the interaction to a first approximation it would be sufficient to consider the influence of the two O^{--} doublets in the same group. Taking R and A to refer to <u>one</u> O^{--} ion, we would obtain after taking the influence of its two neighbours into account

$$R_\varepsilon = \frac{4\pi}{3} N A_\varepsilon \quad ; \quad R_\omega = \frac{4\pi}{3} N A_\omega$$

where $A_\varepsilon = A\left(1 - \frac{2A_\varepsilon}{r_0^3}\right)$

$$= \frac{A}{1 + \frac{2A}{r_0^3}} \quad \text{-------- (1)}$$

where r_0 is the dist between any two O^{--} atoms in the same group.

Similarly $A_\omega = \dfrac{A}{1 - \frac{4A}{r_0^3}}$. ---- (2)

As a second approximation we have to take into consideration also ~~neighbouring~~

atoms in the other groups; and among these it would again suffice to take the O^{--} ions in the ~~neighboring~~ other groups and neglect the influence of the Ca or Na ions either in the same molecule or in surrounding molecules. This latter influence slightly <u>diminishes</u> the effect of the two O^{--} ions in the same group, and its value may again be assumed to be practically independent of r_0. Taking the known values of the distances from one group to another Bragg calculates the latter influence and gets instead of equations (1) and (2) the following expressions.

$$\frac{R_\alpha}{N\times\frac{4\pi}{3}} = \quad A_\varepsilon = \frac{A}{1 + \frac{2A}{r_0^3} - 4\cdot2\times10^{22}\cdot A} \quad \text{---} \;(1')$$

$$\frac{R_\beta}{N\times\frac{4\pi}{3}} = \quad A_\omega = \frac{A}{1 - \frac{A}{r_0^3} + 2\cdot1\times10^{22} A} \quad \text{---} \;(2')$$

$$\frac{1}{A_\varepsilon} + 2\times\frac{1}{A_\omega} = 3\times\frac{1}{A}$$

~~of course~~ $A_\varepsilon + 2A_\omega > 3A$

as we should expect ∴ An increase in anisotropy ~~tends to~~ always gives an increase of refractivity; ~~and~~

Bragg has assumed for the atomic refractivity of O^{--} the value 3·30 which corresponds to

$$\frac{4\pi}{3} N A = 3\cdot30$$

$$A = 1\cdot299\times10^{-24}$$

In the case of $\underline{CaCO_3}$ the difference in molecular refractivities ~~for~~ the ordinary and extraordinary rays is experimentally known to be equal to 13·31 − 10·37

$= \underline{\underline{2{\cdot}94}}$ All this difference is due according to our assumption to the three O^{--} ions so that

$$\frac{4\pi}{3} N \left(A_\omega - A_\varepsilon\right) = \frac{2{\cdot}94}{3}$$

which corresponds to

$$A_\omega - A_\varepsilon = 3{\cdot}86 \times 10^{-25}.$$

or
$$\frac{A_\omega - A_\varepsilon}{A} = \frac{2{\cdot}94}{3 \times 3{\cdot}30}.$$

Writing (1′) and (2′) in the form

$$\frac{A_\omega}{A} = \frac{1}{1-x} \quad \text{and} \quad \frac{A_\varepsilon}{A} = \frac{1}{1+2x}$$

where $x = \frac{A}{r_0^3} - 2{\cdot}1\times10^{22} A$

we can easily determine the value of r_0 which will give the above value of $A_\omega - A_\epsilon$.

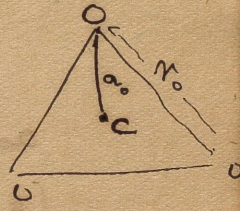
$$\frac{1}{1-x} - \frac{1}{1+2x} = \frac{2{\cdot}94}{9{\cdot}90}$$

$$\frac{3x}{1+x-2x^2} = \frac{2{\cdot}94}{9{\cdot}90}$$

whence $\underline{x = {\cdot}1080}$

$$\therefore \frac{A}{r_0^3} = {\cdot}1080 + {\cdot}0273 = {\cdot}1353$$

whence $r_0 = 2{\cdot}13$ A.U.



The corresponding value of a_0

i.e. the dist. from the C to the O atoms

$$= \frac{2{\cdot}13}{\sqrt{3}} \text{ A.U} = \underline{\underline{1{\cdot}23 \text{ A.U.}}}$$

as against 1·24 A.U given by Bragg.

Similarly for the nitrate ion (in say sodium nitrate) for which the difference in the gm. mol. refractivities for the two rays is equal to 12·58 − 7·75 = 4·83

$$\frac{1}{1-x} - \frac{1}{1+2x} = \frac{4\cdot83}{9\cdot90}$$

whence $x = \cdot1817$

$$\therefore \frac{A}{r_0^3} = \cdot1817 + \cdot0273 = \cdot2090$$

$$r_0 = 1\cdot84 \text{ A.U.}$$

$$\therefore \quad a_0 = 1\cdot06 \text{ A.U.}$$

as against the value 1·09 A.U of Bragg. (There seems to a small error in Bragg's calculation)

For KNO_3 however for which $R_{\frac{\beta+\gamma}{2}} - R_\alpha = 14\cdot22 - 9\cdot90 = 4\cdot32$ (Bragg however gives the value as 4·46 in his Table on p. 353 of his 2nd paper, which is due to an error in his calculation of $R_{\frac{\beta+\gamma}{2}}$), $x = \cdot161$, $r_0 = 1\cdot90$ Å, $a_0 = 1\cdot10$ A.U.

27th Apr. 1930

Potassium chlorate is a monoclinic crystal whose principal ref. indices are for the D line

$\alpha = 1{\cdot}440$, $\beta = 1{\cdot}515$, $\gamma = 1{\cdot}525$

~~As~~ Density = 2·32. Mol. wt = 122·55

The molecular refractivities are therefore equal to

$$R_\varepsilon = R_\alpha = 13{\cdot}93;\ R_\omega = R_{\frac{\beta+\gamma}{2}} = 16{\cdot}05,$$

treating it as a uniaxial crystal, since β and γ are very nearly equal.

The value for $R_\omega - R_\alpha = \underline{\underline{2{\cdot}12}}$ suggests that here also the birefringence may be wholly due to the three O^{--} ions as in the carbonates and nitrates, which is not apriori improbable. Because in the first place we are tempted (from chemical considerations) to assign to ~~the~~ ClO_3^- the simple ~~structure~~

plane symmetrical structure characteristi of CO_3 and NO_3 and secondly the $KClO_3$ crystal resembles strongly in form calcite and $NaNO_3$. In fact Groth (Chem. Krist., 2, 81) remarks regarding $KClO_3$ "die Krystalle sind monoklin, zeigen aber in ihrer ~~gewöh~~ gewöhnlichsten Ausbildung eine grosse Ähnlichkeit mit einem Rhomboëder, und zwar mit demjenigen des Natriumnitrates und dem des Calcits, und diese Ähnlichkeit erstreckt sich auch auf die Cohäsionsverhaltnisse (Spaltbarkeit, Gleitung), und die optischen Eigenschaften (negative Doppelbrechung mit kleinem Axenwinkel, dessen Mittellinie nahezu mit der ~~ps~~ pseudotrigonalen Axe zusammenfällt",

Hence assuming that the birefringence ~~the~~ is due to the plane structure of the ClO_3 ion, Cl^{+++++} contributes very little to the refractivity we can calculate as before the distance (r_0) betn ~~the~~ any two of the O atoms in the group, as also the distance (a_0) from the central Cl.

$$\frac{1}{1-x} - \frac{1}{1+2x} = \frac{2\cdot12}{9\cdot90}$$

whence $x = \cdot077$

$$r_0 = 2\cdot32 \text{ A.U}$$

$$a_0 = 1\cdot34 \text{ A.U.}$$

In the following Table are collected together the various values for the three ions.

	CO_3^{--} ion in $CaCO_3$	NO_3^- ion in $NaNO_3$	ClO_3^- ion in $KClO_3$
$R_\omega - R_\varepsilon$	2·94	4·83 (~~4·46 in KNO_3~~)	2·12
x	0·108	0·182 (~~0·167 for KNO_3~~)	0·077
Dist. from centre to the O atoms } = a_0	1·23 Å X ray data Ca 1·24 Cd 1·23 Mn 1·27 Fe 1·27	1·06 Å Li ~~1·09 (KNO_3)~~ 1·25 Na 1·27	1·34 Å
Ratio of the two polarisabilities of the ion <u>in the crystal</u>* $= \frac{R_\omega}{R_\varepsilon} = \frac{1+2x}{1-x}$	~~1·363~~ 1·36	~~1·667~~ 1·67	~~1·250~~ 1·25
Same ratio for the <u>free ion</u> (e.g. in very dilute solus) $= \frac{1+\frac{2A}{r_0^3}}{1-\frac{A}{r_0^3}}$	~~1·469~~ 1·47	~~1·793~~ 1·79	~~1·348~~ 1·35

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* i.e., as influenced by the doublets induced in the atoms of neighbouring ions in the crystal. The latter tend to diminish the ratio.

28th Apr. 1930.

Bragg's theory of mutual interaction of the doublets suggests a shifting of the natural ultra-violet frequency of the O'' [illegible] in the nitrate or carbonate ion to ~~the~~ longer wavelengths for vibrations in the plane of the ions, and to correspondingly shorter wave-lengths for vibrations perpendicular to the plane. But a little calculation shows that this shifting suggested by Bragg's theory [illegible] is far too small to explain the occurrence of a band at either λ 1940 or λ 3000 ~~as~~ actually observed in the case of the nitrates for vibrations in the plane of the ion.

On Bragg's theory when x in our expression for A_ω (see pp. 24-25) which goes on increasing as we proceed to ~~the~~ shorter wave-lengths, passes through unity, A_ω changes from a large positive to a large negative value, and thus the condition

$$x = 1 \qquad \text{-------} (1)$$

gives the position of the absorption frequency of the NO_3^- ion for vibrations in the plane, while

$$x = -\frac{1}{2} \qquad \text{----} (2)$$

gives the corresponding frequency for vibrations perpendicular to the plane.

Let us first calculate the value of λ_ω given by ~~the~~ (1).

$$x = \frac{A}{r_0^3} - 2.1 \times 10^{22} A = 1$$

which gives (taking $r_0 = 1.84$ Å (see p. 26)),

$$A = 7.14 \times 10^{-24}$$

which corresponds to a value for

the atomic refractivity of the O^{--} equal to 18·1 as against the value 3·30 for the D line.

It is obvious that such a high value for the refractivity of the O^{--} ion (which is more than 5 times the value for the D line) is not likely to be reached except in the close proximity of the natural frequency of the O^{--} ion, which must be in the extreme ultra violet (and nowhere near either 2000 or 3000 A.U.)

In fact it is possible to estimate the rate at which the refractivity of the O^{--} ion varies as we proceed to the ultra-violet. Taking Al_2O_3, the molecular refractivities are for the C line $R_\omega =$ ~~10·46~~ 10·53 $R_\varepsilon = 10·45$ and for the F line $R_\omega = 10·65$ $R_\varepsilon = 10·56$

The increase with diminution of wave length is so small that it is not at all probable that the refractivity for O^{--} will reach as high a value as 18 for even 2000 A.U. ∴ even neglecting the refractivity of the two Al atoms, the three O^{--}'s alone in Al_2O_3 would then (have to possess) ~~give~~ a mol. refractivity of 54 ~~as against~~ which is about 5 times the value in the visible region; while the increase from C to F is only 1 %.

Taking again the SO_4^{--} ion, for which Bragg remarks that the refractivity is due only to the 4 O^{--} ions, we can calculate the natural frequency of the O^{--} ion in the ultra violet by the use of some kind of ~~dispersion~~

dispersion formula. The following table gives the values for H_2SO_4, for which the whole refractivity is due to the SO_4 ion itself.

	λ	n at 23°C $\rho = 1.827$	molecular ~~R~~ refractivity R.	
			Cal.	observed
	μ			
C	·656	1·427	13·77	13·77
D	·589	1·429	13·81	13·83
F	·486	1·434	13·93	13·94
G′	·434	1·437	14·03	14·03

The third column gives the values calculated on the basis of a single frequency dispersion formula of the type

$$R = \frac{13.57 \times \lambda^2}{\lambda^2 - \cancel{.006}\ \lambda_0^2} \quad \text{where } \lambda_0^2 = \cdot 0061$$

λ and λ_0 being expressed in μ's

$$\lambda_0 = \cdot 078\,\mu \qquad \text{i.e. } 780 \text{ A.U.}$$

which is of the same order of magnitude as the ~~freq~~ natural frequency calculated by Cuthbertson from the dispersion of O_2 molecule.

On the basis of the above disper. formula the absorption wave length of the NO_3 ion for vibrations in the plane of the ion is given by (λ being in μ)

$$\frac{13 \cdot 57\,\lambda^2}{\lambda^2 - \cdot 0061} = 18 \cdot 1 \times 4$$

or $\lambda = \cdot 087\,\mu$ or 870 A.U.

ie the shift is only from 780 to 870 A.U. What-ever may be the significance of the absolute values of these wavelengths, they give us an idea of the order of magnitude of the shift of the absorption band to be expected due to the mutual influence of the ~~mole~~ different atoms in the crystals of $NaNO_3$ or KNO_3.

The same shift can also be calculated in a slightly different manner, which offers a check on the previous calculation. Representing the natural frequency of the O'' ion (neglecting influence of its neighbours) as ν_0, and the same ~~aft~~ ~~for~~ [illegible] after taking the influence into account, by ν_ω and ν_ε for vibrations in the plane and $\perp^r$ to the plane of the NO_3 ion,

$$A = \frac{C}{\nu_0^2 - \nu^2}$$

$$A_\omega = \frac{C}{\nu_\omega^2 - \nu^2}$$

$$A_\varepsilon = \frac{C}{\nu_\varepsilon^2 - \nu^2}.$$

Also we have the relation

$$\frac{2}{A_\omega} + \frac{1}{A_\epsilon} = \frac{3}{A}$$

Now for the sodium line we have seen that for the nitrate ion

$$\frac{A_\omega}{A_\epsilon} = 1{\cdot}67$$

Whence we get

$$\frac{\nu_\omega^2 - \nu^2}{\nu_0^2 - \nu^2} = \frac{3}{3{\cdot}67}$$

whence $\lambda_0 = 780$ A.U.

λ_ω comes out again as $\underline{\underline{870 \text{ A.U.}}}$

Thus the theory of Bragg can not in any way explain the presence of the two absorption bands for NO_3 at λ 2000 and λ 3000 for vibrations in the plane of the ion.

Let us now proceed to discuss critically whether the mutual interaction theory of Bragg explains at least the birefringence of NO_3 or CO_3 consistently for different wave-lengths. The ~~ex~~ success claimed by Bragg for the D line does not mean very much since both the molecular refractivity of O^{--} and the ~~[illegible]~~ dist. betw the O atoms in the group are both adjustable; Bragg assumes certain reasonable values for the refractivity and gets values for r_0 ~~which are~~ about which it can only be said that they are not improbable. Now having determined ~~[illegible]~~ the value of r_0 let us calculate the values of the refractivity of O^{--} that base to be assumed in order to explain the birefringence of NO_3 or CO_3 for different wave-length. We shall take $CaCO_3$ since it has been studied thoroughly for its refractivity over a very wide range of wave-lengths.

Taking the refractive index for the shortest wave-length for which measurements have been taken viz

for Aw $\cdot 200\,\mu$ $\quad \omega = 1{\cdot}90284$ $\quad \epsilon = 1{\cdot}57649.$ $\Big\{$ for calcite. Martens, Landolt-Tables.

$$R_\omega = 16{\cdot}85 \qquad R_\epsilon = 11{\cdot}96$$

$$R_\omega - R_\epsilon = 4{\cdot}89$$

Corresponding to this birefringence, for the $\bar{O}$ ion, $A_\omega - A_\epsilon = 0{\cdot}642 \times 10^{-24}$.

$$\text{Now} \quad A_\omega = \frac{A}{1 - \frac{A}{r_0^3} + 2{\cdot}1 \times 10^{22} A}$$

Taking for calcite $r_0 = 2{\cdot}13$ A.U (p. 25)

$$\cancel{A_{\omega\varepsilon} = \frac{A}{1-\cdot 6}}$$

$$A_{\omega} = \frac{A}{1 - \cdot 083 \times 10^{24} A}$$

$$A_{\varepsilon} = \frac{A}{1 + 2 \times \cdot 083 \times 10^{24} A}$$

For the above value of $A_{\omega} - A_{\varepsilon}$ we get

$$A = 1\cdot 685 \times 10^{-24}$$

~~as~~ which corresponds to an atomic refractivity for the O^{--} ion ~~wh~~ equal to

$$\underline{\underline{4\cdot 28}} \quad \text{for } \lambda = 2000 \text{ A.U.}$$

as against 3·30 for the D line.

The value seems to be reasonable since the dispersion formula (on p. 37) ~~for~~ for H_2SO_4 gives for this wave-length

$$R_{H_2SO_4} = 16\cdot 01 = \underline{\underline{4 \times 4\cdot 00}}.$$

and the difference is of the same order

as that found between the values for the refractivity of O^{--} calculated from different compounds.

~~Similarly~~ the refractive indices of calcite for the H line (·397 μ) are

$\omega = 1{\cdot}683 \quad \varepsilon = 1{\cdot}498$.

$R_\omega = 13{\cdot}71$

$R_\varepsilon = 10{\cdot}59 \qquad R_\omega - R_\varepsilon = 3{\cdot}12.$

Assuming the value of r_0 which we have already calculated from the known birefringence of the crystal for the D line, viz. $r_0 = 2{\cdot}13$ Å.U, we can calculate the atomic refractivity of O^{--} (for the H line) necessary to explain the above value of $R_\omega - R_\varepsilon$ and this comes out as

$$R = 3{\cdot}39$$

as against 3·30 for the D line

which is of the right order of magnitude judging from the dispersion of ~~[illegible]~~ feebly birefringent oxides like Al_2O_3 or SiO_2, or from the dispersion of H_2SO_4.

If now we calculate the atomic refractivity of $O^{''}$ for the H line from the birefringence of ~~[illegible]~~ $NaNO_3$, using $r_0 = 1.84$ A.U. (calculated from ~~[illegible]~~ $\omega - \varepsilon$ for the D line), in exactly the same manner as for calcite, we get

$$R_\omega = 13.25 \quad R_\varepsilon = 7.93$$

$$R_\omega - R_\varepsilon = 5.32$$

whence R for $O^{''}$ = 3.46

as against 3.39 from Calcite.

3rd May 1930

The explanation of the failure of Bragg's theory to ~~expl~~ predict the positions of the ultra violet absorption bands of the NO_3 group, while it gives reasonable values for the birefringence of $CaCO_3$ up to even 2000 A.U. and for $NaNO_3$ in the visible region, is probably as follows:- ~~Just as~~ When we are working in a region of the spectrum *sufficiently* removed from the ultra-violet natural frequencies, assumed to be more than one, the refractive index will be given correctly to a first approximation, by the assumption of a *single* effective ultra-violet frequency, while when we go nearer and nearer towards the ultra violet frequencies, the value of the ref. index calculated on the assumption of the above single ultra violet frequency will be smaller and smaller, ~~with~~ in comparison with the actual ref. index; for a correct calculation we have to know the actual frequencies, especially of the [illegible] absorption band of longest wave length, (which would be nearest to it) even though the contribution of this particular band to refr. index in the visible region may be quite small in comparison with the contribution from ~~the~~ others in the more remote ultra violet.

In the same manner in calculating the birefringence of the NO_3 or CO_3 ion, as long as we are working in a region so far removed from the ultra violet—

frequencies of the ~~three O^{--} ions~~ different dispersing electrons in the NO_3 group, that the (numerical value of the) induced moment due to any one of them (expressed in C.G.S., E.S. Units) is small in comparison with the cube of the distance (expressed in cms.) of the ~~electr~~ particular doublet, from its nearest neighbour, then the field due to mutual influence is small, in comparison with the inducing field, and ~~a~~ so far as the calculation of the birefringence due mutual interaction of the various doublets are concerned, we can treat ~~them~~ as though they are concentrated in a few localised centres; for instance in the case of ~~the nitr~~ NO_3 and CO_3, owing to the trigonal symmetry in the plane of the ions, in three points at the corners of an equilattriangle, each such group of electrons is isotropic contributing a certain definite amount to the refractivity, the birefringence arising from the mutual influence.

But when we proceed to the ultra-violet as soon as the moment induced of the doublet ~~induced in one~~ due to any two neighbouring dispersing electrons ~~becomes equal to~~ in the plane of the NO_3 or CO_3 group, say A and B, are ~~such the~~ sufficiently high that

$$4AB = r^6$$ where r is the dist. between them (all the other electrons are supposed to be at greater distances) then the ref. index tends to become very large and there will be an absorption band due to interaction.

4th May 1930

P. G. Tait in the course of a letter to Stokes under date 2-1-90 writes

" When you have leisure, I should like much to know what you think is the cause of the WHITENESS of snow, as seen on a dark night far from any terrestrial source of light and when the only illumination is from clouds which seem (at least) not white nor neutral grey, but INDIGO. Is snow a fluorescent substance? I have thought of this every winter for several years: but I have never had a really satisfactory trial with a spectroscope. When observations have been possible, I have always been unable to get into a part of the country where they could properly be made. But on two or three occasions, when I was obliged to be out long before sun-rise, but after the gas-lights were out, the contrast of tint between the snow and the cloud-hemisphere has much impressed me." — "Sir George Gabriel Stokes: Memoir and Scientific correspondence" Camb. Univ Pres. 1907, Vol II, p. 132.

6th May, 1930

I. Maslakowez (Zs. Phys. 51, 696, (1928)) has investigated the absorption spectrum of KNO_3 and KNO_2 in the ultraviolet and in the infra red regions of the spectrum. ~~both~~ ~~They~~ He used the substances in the form of thin layers deposited on a quartz plate by allowing a layer of dilute soln. to evaporate; he has also studied them in solution in water. He obtains in solution, for KNO_3 two ultraviolet bands one at about 300 mμ and another which is very much stronger at 206 mμ.

& for KNO_2 a band at 360 mμ which is much stronger than the corresponding band of KNO_3 at 300 mμ, and another at 206 mμ which is considerably stronger than the one at 360 mμ but weaker than the corresponding band for KNO_3.

the 206 mμ band for the nitrite seems to be accompanied by a close satellite ~~at~~ whose max. lies somewhere between 210 mμ and 220 mμ (say, at 215 mμ)

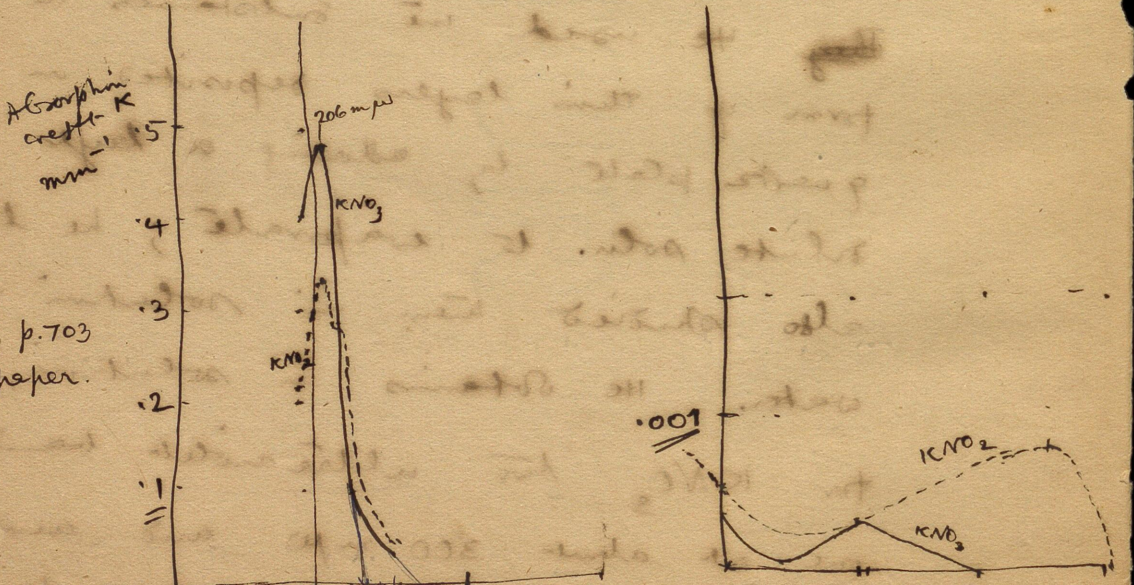


Fig 11, p.703 of his paper.

Concentration = ·0017 %

		thin crystal layer	soln.	
KNO_3	$\frac{K_{206}}{K_{300}} =$	$\frac{20}{1}$	$\frac{1500}{1}$	$= \frac{\cdot 48}{\cdot 00032}$
KNO_2	$\frac{K_{206}}{K_{360}} =$	$\frac{8}{1}$	$\frac{400}{1}$	$= \frac{\cdot 33}{\cdot 0008}$

$$\frac{K_{360} \text{ of } KNO_2}{K_{300} \text{ of } KNO_3} = 2{\cdot}5 \quad // \text{ roughly for the solution.}$$

7th May 1930

The absorption coeff— k in the above table (& figs) is defined by

$$K = \frac{1}{d} \log_e \frac{I_0}{I}$$

where d is expressed in millimetres

NB

Thus for the soln of concentration

= ·0017 gms in 100 gms of water (or soln)

K = ·48 per mm for 206 mμ and

is equal to ·00032 for 300 μμ.

The absorption coeffts ε given by Halban, Schäibe, Morton and others are defined by

$$\log_{10}\frac{I_0}{I_d} = \varepsilon c d$$

where d is the thickness in cms
c is the concentration expressed in mol. per litre of solution
and the log of I_0/I is to the base 10

On this latter unit Morton gives ε for the NO_3 ion in very dilute solns for the 300 mμ band as ~~to~~ 7·2, and for the 200 mμ band Schäibe gives it as 12,000. [Morton in his R.S paper 113, 729, wrongly quotes the

55

value as 1202]. Whereas the curves of Maslakowez would give

$$\cdot 00032 \times \frac{10 \times \overset{101\cdot 1}{\cancel{62}}}{\cdot 0017 \times 10^{4}} \times \log_{10} e \quad \times \frac{[illegible]}{62}$$

$$= \cancel{\cdot 00032 \times 1\cdot 58 \times 10^{4}} \times \frac{101\cdot 1}{6} = \overset{8\cdot 3}{\cancel{5\cdot 1}} \text{ for } 300\,m\mu$$

$$\cancel{\text{and } \cdot 48 \times 1\cdot 58 \times 10^{4}} = \overset{12,400}{\cancel{7600}} \text{ for } 200\,m\mu$$

For crystal (of density 2·11) absorption coefft K for 300 μ band defined by $I = I_0 e^{-Kd}$ where d is in cms. $\doteq$ 397.

8th July 30.

On the widening of the absorption lines of alkaline metallic vapours.

Let us first consider the case of two optically isotropic atoms at a distance d apart. Let μ the moment induced in each of the atoms by unit field of a light wave when the other atom is removed to infinity. If now the second atom is brought to its original position the moment induced will no more be equal to μ but will depend on the direction of the incident field. ~~The~~ When the latter is along the line joining the two atoms, the moment induced in either of the atoms will be given by

$$\mu_{\parallel} = \mu\left[1 + \frac{2\mu_{\parallel}}{d^3}\right]$$

$$= \frac{\mu}{1 - \frac{2\mu}{d^3}} \quad \text{- - - -} \ (1)$$

and the corresponding frequency of absorption will be given by the relation $\mu_{\parallel} = \infty$ ie $\frac{2\mu}{d^3} = 1$ - - (2)

whereas for the isolated atom it is given by $\mu = \infty$.

On the other hand when the field of the incident light-wave is $\perp^r$ of the incident light-wave is $\perp^r$ to the line joining the two atoms the moment induced is given by

$$\mu_{\perp} = \frac{\mu}{1+\frac{\mu}{d^3}} \quad - - - - (3)$$

and the absorption frequency is given by the condition

$$\frac{\mu}{d^3} = -1 \quad - - - (4)$$

Now let us calculate the change in frequency for the case of say two sodium atoms at a distance d_0 apart. It is evidently necessary to know the dispersion of μ, which is easily calculated from the measurements on the refractive index of a rare vapour for different wave-lengths. Thus Wood finds that for saturated Na vapour at 644° C. the refraction can be expressed by the formula

$$n^2-1 = \frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{m_2\lambda^2}{\lambda^2-\lambda_2^2} + \frac{m_3\lambda^2}{\lambda^2-\lambda_3^2} +$$

where each term corresponds to one of the members of the principal series, beginning with the first.

Taking the absorption of the first member, we may neglect the other terms, and we get the simple relation

$$n^2-1 = \frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} \quad ---(6)$$

and in view of the well-known relation for a rare vapour, viz.,

$$n^2-1 = 4\pi N\mu \quad --(7)$$

where N is the no. of atoms per unit vol. of the refracting vapour we get the ~~necessar~~ dispersion of μ.

Let the absorption be given

-(5) by $\lambda_1 + \Delta\lambda_r$ ~~=~~ for $\|^l$ vibrations where the shift would evidently be to the red side of the spectrum. For this wave length $\frac{2\mu}{d^3}$ should be equal to unity; and we thus obtain

$$\frac{2\cancel{\mu}}{d_0^3}\times\frac{n^2-1}{4\pi N} = 1$$

$$\text{or} \quad \frac{2}{d_0^3}\cdot\frac{1}{4\pi N}\times\frac{m_1\lambda^2}{2\lambda\Delta\lambda_r} = 1$$

i.e. $$\frac{\Delta\lambda_r}{\lambda} = \frac{m_1}{4\pi N d_0^3} \quad \text{------(8)}$$

~~Thi~~ Similarly we get for the shift of the absorption wave length for $\perp^r$ vibrations (the shift would now be on the violet side) the value

$$\frac{\Delta\lambda_v}{\lambda} = -\frac{m_1}{8\pi N d_0^3} \quad \text{-----(9)}$$

~~Taking for the case~~ If the distance betw the two sodium atoms is the same as the dist. of closest approach in sodium crystal, then

$$d_0 = 3.7 \text{ A.U.}$$

For the saturated vapour at 644°C Wood gives the value of m_1 as 5.5×10^{-5} [Both in his original paper in Phil. Mag. 1904, and more recently in his book on physical optics Wood gives indiscriminately both the values $5{\cdot}5 \times 10^{-5}$ and $5{\cdot}5 \times 10^{-4}$ in several places! On actual calculation from the experimental values of the refractive index quoted by him the former value viz $5{\cdot}5 \times 10^{-5}$ ~~appears to be the~~ is found to be the correct one. [Also he occasionally writes $n-1$ where he should have used n^2-1]

Regarding the Saturation pressure at 644° C. if we assume that Ladenberg's formula [quoted in Landolt Tables

$$\log p\,(\text{mm}) = -\frac{26420}{4{\cdot}571\,T} - 1{\cdot}178\log T + 11{\cdot}435$$

which is found to hold over the ~~to~~ range 350°C to 570°C. can be extrapolated for 644°C then we get—

$$p = 44 \text{ mm}.$$

On the other hand if we

the empirical formula given by W. H. Rodebush and T. De Vries (Journ. Am. Chem. Soc., 47, 2488 (1925)) viz.

$$\log p\,(\text{mm}) = -\frac{5922}{T} - 1.6184 \log T + 12.9605$$

which he finds valid betw 514°C. ~~to~~ and the boiling pt. 883°C. then we get $p = 52$ mm.

The empirical formula given in the International Crit. Tables gives the value 47 mm. which is roughly the mean of the above two and may be adopted

The corresponding value of N would be ~~5.0×10^{17} per c.c.~~

$$\frac{6.062 \times 10^{23}}{22.4 \times 10^{3}} \times \frac{47}{760} \times \frac{273}{917}$$

$= 5.0 \times 10^{17}$ per c.c.

using these values we have from (8) and (9)

$$\frac{\Delta\lambda_r}{\cancel{\Delta}\lambda} = \frac{5.5\times10^{-5}}{4\pi\times5.0\times10^{17}\times3.7^3\times10^{-24}}$$

$$= 0.17$$

and $$\frac{\Delta\lambda_v}{\lambda} = -0.09.$$

~~ie.~~ Since $\lambda = 5893$ A.U.

$\Delta\lambda_r$ is roughly 1000 A.U.

while $\Delta\lambda_v$ would be 500 A.U.

The values can also be calculated rigorously. The limit of broadening on the red side will be given by the condition $2\mu/d_0^3 = 1$

i.e. $$\frac{2}{3.7^3\times10^{-24}} \times \frac{5.5\times10^{-5}}{4\pi\times5.0\times10^{17}} \cdot \frac{\lambda_r^2}{\lambda_r^2-\lambda_0^2} = 1$$

i.e. ~~$\frac{\lambda_r^2}{\lambda_r^2 - \lambda_0^2}$ = ·3457 0·35~~ i.e. $\frac{\lambda_r^2 - \lambda_0^2}{\lambda_r^2} = \cdot 35$

$\therefore \lambda_r = 7285$ A.U

$\Delta\lambda_r = \underline{\underline{1390}}$ A.U.

Similarly $\frac{\lambda_0^2 - \lambda_v^2}{\lambda_v^2} = \cdot 17$

$\lambda_v = 5440$ A.U.

$\therefore \Delta\lambda_v = \underline{\underline{450}}$ A.U.

65

9th July 1930

For very closely packed sodium atoms

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} N \mu \omega = K \text{ say}$$

n^2 is negative for positive values of K greater than 1 and negative values numerically greater than $-\frac{1}{2}$. Interpreting the negative values of ~~k~~ n^2 as indicating metallic absorption, the absorption will extend on the longer wave length side to a wave length for which $K = 1$

i.e. $$\frac{4\pi}{3} N \times \frac{n^2-1}{4\pi N_0} = \frac{N}{3} \times \frac{m_1 \lambda^2}{N_0 \lambda^2 - \lambda_0^2} = 1$$

i.e. $$\frac{N}{3} \times \frac{5.5 \times 10^{-5}}{5.0 \times 10^{17}} \cdot \frac{\lambda^2}{\lambda^2 - \lambda_0^2} = 1$$

Now the density of solid sodium = ·97 which would correspond to $N = \dfrac{6.06\times10^{23}}{23.0}\times{\cdot}97$ atoms per c.c. In general

~~Now~~ $$N = \frac{6.06\times10^{23}\ \cancel{\times{\cdot}97}}{23.0}\times\theta$$

where θ represents the density as a fraction of that of the solid.

$$\therefore\ \cancel{\frac{\lambda^2}{\lambda^2+\lambda_0^2}}\ \frac{\lambda_v^2-\lambda_0^2}{\lambda_v^2} = \frac{5.5\times10^{-5}\times6.06\times10^{23}\times{\cdot}97\,\theta}{3\times5.0\times10^{17}\times23}$$

$$= {\cdot}938\ \theta.$$

for ~~[illegible]~~ extension on the shorter wave length

$$\frac{\lambda_0^2-\lambda_v^2}{\lambda_v^2} = 1.876\ \theta.$$

1) let $\theta = 1/25$

$$\frac{\lambda_r^2 - \lambda_0^2}{\lambda_r^2} = .0375$$

$$\lambda_r^2 = \frac{\lambda_0^2}{.9625}$$ Takg $\lambda_0 = 5893$ AU

$$\lambda_r = 6006 \text{ AU}$$

$$\Delta\lambda_r = \underline{\underline{113 \text{ AU}}}.$$

$$\frac{\lambda_0^2 - \lambda_v^2}{\lambda_v^2} = .0750$$

$$\lambda_v = \frac{5893}{\sqrt{1.075}} \text{ AU} = 5683 \text{ AU}$$

$$\Delta\lambda_v = \underline{\underline{210}} \text{ Å}$$

$$\Delta\lambda = 323 \text{ Å}$$

2) let $\theta = 1/10$

$$\lambda_r = \frac{\lambda_0}{\sqrt{\cdot 9062}} = 6190 \text{ Å}$$

$$\underline{\underline{\Delta\lambda_r = 297 \text{ Å}}}$$

$$\lambda_v = \frac{\lambda_0}{\sqrt{1\cdot 188}} = 5406 \text{ Å}$$

$$\Delta\lambda_v = 487 \text{ Å}$$

$$\Delta\lambda = \underline{\underline{784 \text{ Å}}}$$

3) let $\theta = 1$

$$\lambda_r = \frac{\lambda_0}{\sqrt{\cdot 062}}$$ ~~[illegible]~~ very large

$$\lambda_v = \frac{\lambda_0}{\sqrt{2\cdot 876}} = 3474 \text{ Å}$$

11th July, 1930

Wave Lengths of the 1st members of the principal series of some metals

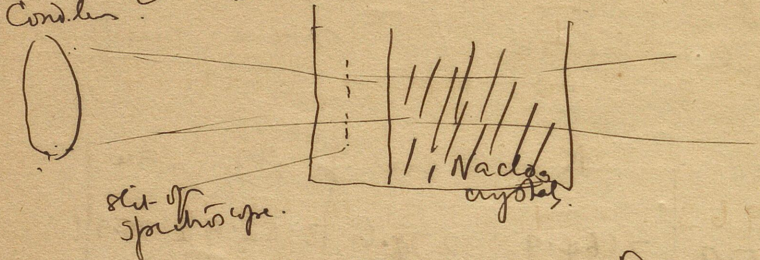
metal.	Na	K	Cu	Ag	Au
λ in A.U.	5895·9	7664·9	3274·6	3382·9	2675·9 ?
	5890·0	7699·0	3247·6	3280·7	2428·0

the.

using a film of silver chemically deposited on a quartz plate, through which the sun when viewed directly can be just seen, blue, but which is too thick to visibly transmit skylight, Ernst ~~K~~ v. Angerer finds, (~~that~~ using directly bright skylight as the continuous source) that the maximum of transmission occurs at about 3250 A.U.

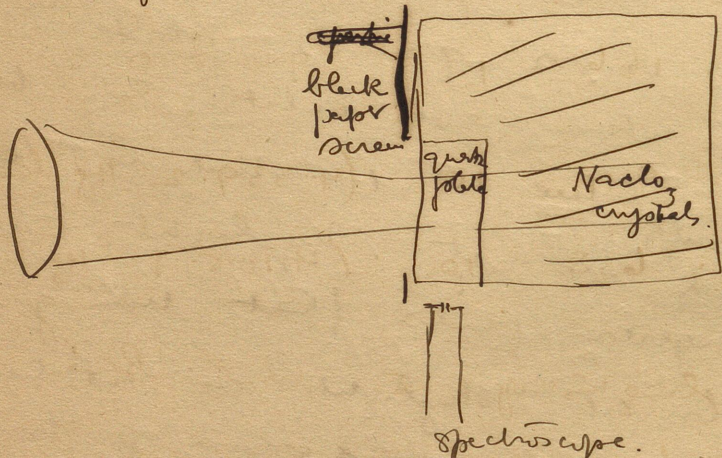
14th July 30

quartz plate thickness. 1 cm. about 2½" cms by 2½ cms. cross section.



Front view.

view from above



$$\lambda = 1379.5 + \frac{\text{antilog. } 5.2670738}{162.404 - n}.$$

Readings on the microscope of the lines appearing on the plate

I

110·752	10	Hg line (4960·4)
103·963	1	4544·4
103·129	0	4499·8
102·693	0	4477·1
102·166	1	4450·0
99·911	10	(4339·2 Hg line)
94·638	10	(4108·9 Hg line)

The wave lengths of the new lines were calculated by using the mercury lines as standards.

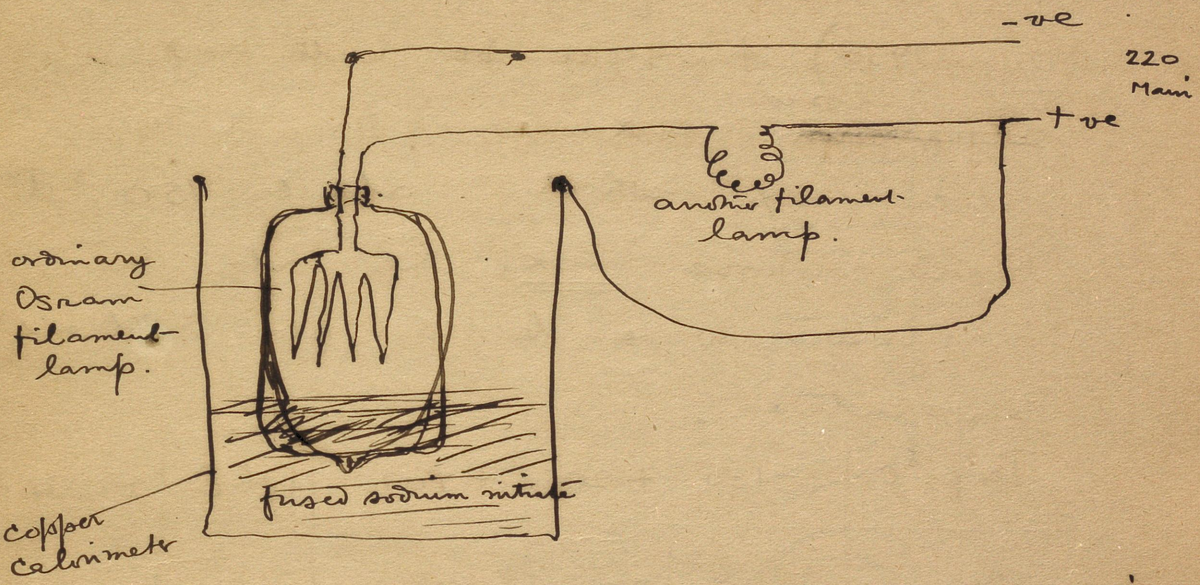
The shifts from the exciting line are 473 (1) 609 (0) 722 (0) 940 (1) per cm. The numbers within brackets give the intensity.

Of these 473 and 722 belong to quartz [Cabannes' values are 467 and 700] and 940 and 609 to $NaClO_3$. [Dawe's values are 936 and 625.].

73

2nd Aug. 1930

Electrolysis of glass.



a good mirror of sodium is deposited inside the bulb in about 10 minutes

4th Aug 30

Lord Rayleigh (Proc. R.S., A, 128, p131 Aug 1930) finds a ~~dc~~ well defined transmission ~~absorption~~ maximum for a thin silver leaf which is about 150 A.U. broad whose max. lies at the following wave-lengths at different temperatures.

Temp °C.	−180	+ 20	+ 107	+160	+254
λ_{max} of transmission	3180	3200	3240	3250	3300

75

5th Aug. 30

Principal series of some of the alkali metals.

I. Å.

m =	2	3	4	Limit of the series
Na.	5895·9 5890·0	3302·9 3302·6	2853·0 2852·8	2412·6.
K	7664·9 7699·0	4044·3 4047·6	3446·5 3447·5	2856·7
Rb.	7800·2 7947·6	4202·0 4215·7	3587·2 3591·7	2968·7
Cs.	8521·2 8943·6	4555·4 4593·3	3876·4 3888·7	3184·0.

Copper.

$$m = 2 \qquad \begin{cases} 3247{\cdot}7 \\ 3274{\cdot}6 \end{cases}$$

$$m = 3 \qquad \begin{cases} 2024{\cdot}4 \\ 2025{\cdot}9 \end{cases}$$

Silver

$m = 3$ 3382·9

3280·7

12th Aug 1930

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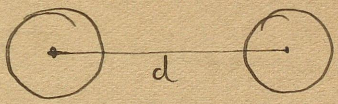
22nd Aug. 1930



Assum~~ing~~ that there are two spherically symmetrical atoms at a distance d apart. Let each of them have a characteristic frequency ν_0 which would ionize it, when the other is removed to infinity, only one electron in the atom taking part in the ionisation. Then when the second atom is brought to position the frequency for vibrations along the nucleus would be diminished to the new value ν given by

$$\frac{e^2}{4\pi^2 m}\cdot\frac{1}{r^3}\cdot\frac{1}{\nu_0^2-\nu^2}=\frac{1}{2}.$$

$h(\nu_0-\nu)$ will give the energy of

dissociation of the molecule into 2 unionised atoms, d represents the distance between the two atoms.

18th Oct. 30.

The ellipticity of light reflected from the surfaces of liquids at the Brewsterian angle.

Liquid.	$+\eta \times 10^5$ Ramdas.	Bouhet.	Ref. index.
methylene iodide		221.0	1.750.
Bromonaphthalene		139	1.668
Benzene	107	132	1.509
Para xylene		129	1.503
Ortho xylene		127.5	1.512
CCl_4	84	126	1.468
Quinolene		126	1.637
meta xylene	202	124	1.502
Cyclohexane		121	1.430
Dibromethylene		114	1.544
Octyl alcohol		101	1.426
Ethyl acetate		99	1.376
Ethyl benzoate		96	1.551
Propionic acid		95.5	1.389
Ethyl alcohol	66	92	1.363
Oleic acid	210	91.5	1.465
Palmitic acid	190		

Liquid ~~Nitrobenzene~~	$+\eta \times 10^5$ Ramdas	Bonhet	Ref index
Nitrobenzene	131	76	1·561
Glycerine		63	1·473
Water	75	40 42 (Rayleigh)	
Methyl alcohol	69		
n. propyl "	90		
iso propyl "	100		
n- Butyl "	92		
iso butyl "	87		
Allyl	110		
β iso Amylene	150		
Pentane	170		
Octane	66		
Acetone	81		
CS_2	142		
Toluene	194		

Birefringence of KNO_3

$\beta - \alpha$ ~~$\alpha - \beta$~~ was measured by placing a thin plate of the crystal parallel to b (010) plane between crossed nicols and analysing the transmitted light with a spectroscope. (see p. 10)

Measurements were repeated ~~made~~ with two more crystals one of thickness

2nd crystal

$t =$ ~~47·829μ~~ x 482·9 μ

Corresponding to dark lines on the -ve of the photographic plate, [whose positions were measured]

$$(\beta - \alpha) t = (2N+1) \lambda/2$$

where $N = n$ given in graphs I (a) & I (b) plus 108.

3rd crystal

The second crystal used was of thickness

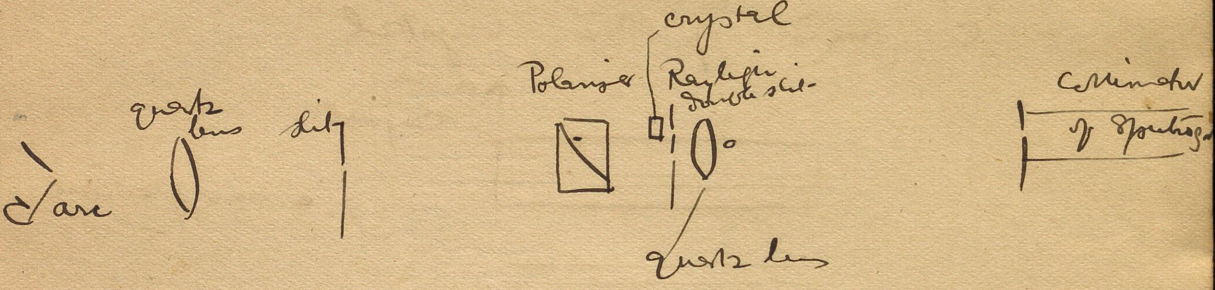
$$t = 68.28\ \mu$$

N in the formula = n plotted in graphs II (a) and II (b) plus 20.

The values of $(\beta - \alpha)$ are collected below:—

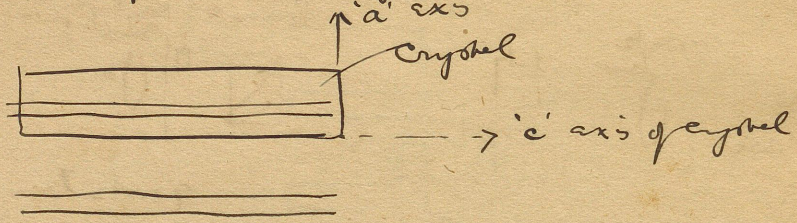
λ A.U	I crystal $t = 614\mu$ $N = n + 147$ $\beta - \alpha =$ another on same crystal $t = 616\mu$ given in ~~brackets~~ by ⊙.	II crystal. $t = 482.9\mu$ $N = n + 108$ $\beta - \alpha =$	III crystal $t = 68.28\mu$ $N = n + 20$ $\beta - \alpha =$	Schrauf.
6868 (B)	(·1664)	·1664	—	·1660
5893 (D)	·1712	·1712		·1710
5270 (E)	·1759 ⑥	·1757	·1752	·1759
4358	·1870 (69)	·1871	·1877	—
3969 H	(·1952) ㊻	·1952	·1956	·1949
3663	·2039 ⑨	·2044	·2044	-
3500		·2106	·2122	
3376	·2157			
3300	~~·2204~~	·2204	·2207	
3100	·	·2340	·2348 -	
2952	- - - -	- - - -	·2495	
2900		··	·2549	
2700			·2868	
2530			·3354	·

Measurement of Absolute ref Indices



A Rayleigh ~~and~~ double slit refractometer was arranged with the crystal in the path of one of the beams. The slits were all horizontal and the horizontal fringes were focussed in the plane of the vertical slit of a quartz spectrograph.

1) incident vibrations $\parallel^l$ to the 'c' axis of the crystal



Ref index measured is $\underline{\underline{\alpha}}$.

Two crystals were used for measurement.

$\underline{\underline{1^{st}\text{ crystal}}}$ $t = 70.75\ \mu$.

see graphs $\overline{\underline{III}}$ (a) and $\overline{\underline{III}}$ (b)
Taken on 2 different plates one for longer wave lengths & other with heavier exposure for shorter wave lengths —

$\underline{\underline{2^{nd}\text{ crystal}}}$ $t = 121.8\ \mu$.

see graphs $\overline{\underline{IV}}$ (a) and $\overline{\underline{IV}}$ (b) α

λ	1st crystal t = 70·7570	graphs IV(a) & IV(b) II crystal t = 121·870	Schrauf.
(B) 6868	1·3310 !		— 1·3328
D 5893	(1·3348)	1·3354 ?	— 1·3346
E 5270	1·3359 ⑥	(1·3366)	— 1·3365
4358	1·3406 ⑩	1·3410	
H 3969	(1·3433) ㊱	(1·3435)	- 1·3436
3663	1·34~~74~~ 48 (70)	1·3459	
3580	1·3483 ⑨	1·3477	
3300	1·3512 ⑳	1·3498	
3100	1·3540 (60)	1·3523	
2952		1·3553	
2900	1·3570	1·3564	
2847	1·3581		
2755		1·3597	

More reliable than measurement on 1st crystal. Adopt.

~~β~~

α

~~λ~~.

λ	with the 2nd crystal of the previous page, and then exposure was taken $t = 1209 \times 10^3$ Å
3663	(1.3459)
3500	79
3300	99
3100	528
2952	51
2900	60
2755	(97)
2700	614
2524	80

(Graphs VI(a) & VI(b)

β.

λ Å \ t =	$t = 118.6\,\mu$. graphs Va & Vb β	$t = 69.43\,\mu$ graph VII.
5270	(1.5125)	
4358	279	
3969	(384)	
3663	503	(1.5501)
3500	578	·586
3300	702	(~~6~~704)
3100		861
2952		995