The optical determination of the relative abundance of isotopes

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THE OPTICAL DETERMINATION OF THE RELATIVE ABUNDANCE OF ISOTOPES.

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PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKS-UNIVERSITEIT TE UTRECHT OP GEZAG VAN DEN RECTOR-MAGNIFICUS
Jhr. Dr. B. C. DE SAVORNIN LOHMAN
HOOGLEERAAR IN DE FACULTEIT DER RECHTSGELEERDHEID VOLGENS BESLUIT VAN DEN SENAAT DER UNIVERSITEIT TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP MAANDAG 17 NOVEMBER 1930 DES NAMIDDAGS TE 4 UUR DOOR

ARTHUR ELLIOTT

GEBOREN TE CLEADON

DRUKKERIJ G. J. WILLEMSE, DOMPLEIN 11 UTRECHT.

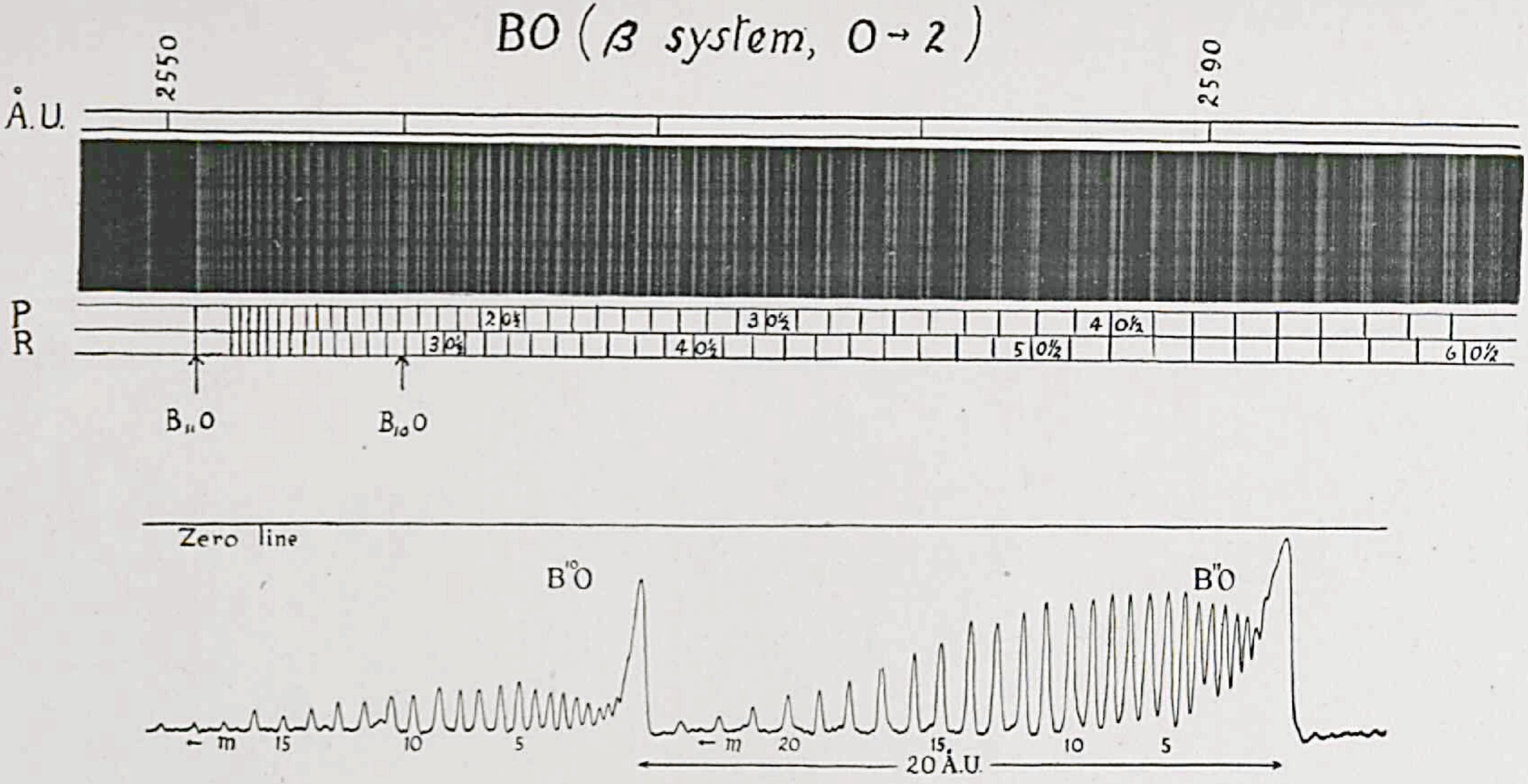

Plate I — Above, 0—2 band of BO in arc.

Below, Photometric Registration of 2—6 band of BO excited by Active Nitrogen.

To my Mother.

The writer has received so much help and kindness during the course of two years in Utrecht that it would be impossible to thank everyone separately; there are, however, several to whom he is especially indebted, and he takes this opportunity of thanking them.

Professor Ornstein, in particular, has been most kind in giving his valuable assistance at all times, and in placing the facilities of his laboratory at his disposal. His friendly interest in matters other than those directly concerned with scientific work have been greatly appreciated.

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CHAPTER I.

The Isotope Effect in Optical Spectra.

Introduction.

The possibilty that elements of identical chemical properties may have different atomic weights was first revealed in the domain of the radio-active elements. Somewhat later, observations by Sir J. J. Thomson showed that the positive rays of neon were not homogeneous, and behaved as if they consisted of a mixture of particles of masses 20 and 22 times that of the hydrogen positive ray.

Subsequent researches of Aston with the mass spectrograph have shown that very many of the elements are not homogeneous, but consist of two or more constituents of different mass; the name "isotopes" has been given to these constituents. All attempts to separate isotopes chemically have failed; they appear to have identical chemical properties. Physical methods, such as diffusion (where the difference in mass gives rise to a difference in the rate of diffusion) have succeeded in partially separating isotopes in a very few cases, but the separation achieved is very small. Isotopes are interpreted as atoms in which the net nuclear charges (and for neutral atoms, the sum of the extra-nuclear electronic charges) are identical. Since the masses differ, we must suppose that the nucleus of one isotope contains more protons than the other, and that the extra protonic charges are neutralized by the same number of electrons in the nucleus.

Much interest has centred around the spectra of isotopes, and much work has been done with a view to establishing the existance of an "isotope effect" in spectra. In what follows, a brief summary of the results hitherto achieved is given.

Atomic Spectra.

Several investigations have been carried out in an endeavour to find a difference between the atomic spectra of isotopes (see (1) for referances), but only in the elements lithium, neon, lead and thallium has anything been observed which may be attributed to an isotope effect.

The first to find a definite displacement of a line when different isotopes of the same element were investigated appears to have been Aronberg, (2) who found that the wavelength of the $\lambda = 4508$ Å. U. line was slightly less in ordinary lead than in radium lead.

The displacement, though small, is however many times that required by the theory, assuming that the effect may be calculated in the same way as in ionized helium, and has not yet been accounted for.

The resonance line of lithium ($\lambda = 6708$ Å.U.) has frequently been examined for an isotope, and indeed a weak companion has been found on the long wave-length side by Schüler and Wurm (3).

This is attributed by them to an isotope effect, and it is suggested that the observed companion is the weak component of the Li^6 doublet.

In the case of neon, more extensive observations and measurements have been made. All the lines which have an *s*-term as the ground term have been found to possess a faint satellite, and Hansen (4) has pointed out that the separation is not greatly different from what would be expected if the satellite were due to Ne^{22}.

Further observations have been carried out by Nagaoka and Mishima (5) and by Thomas and Evans (6).

The former workers showed that every strong line in the yellow and red portions of the spectrum of a neon tube (cooled in liquid air to reduce the width of the lines) shows the faint companion, and further that the separation is nearly constant for lines of the same series, and a little greater than is required by Bohr's formula (7). They also examined the Zeeman effect of the lines, and found that the same effect is shown by the strong lines and satellites. The separations of the satellites have also been measured by Thomas and Evans, and similar values arrived at. The expected intensity ratio is 9 : 1, and eye estimates place it at from 4 : 1 to 10 : 1.

On the whole, the evidence for attributing the satellites to Ne^{22} appears to be very satisfactory.

Molecular Spectra.

Since isotopes have identical extra-nuclear structure, and only differ in nuclear mass and perhaps also in nuclear spin, we should naturally expect to find more evidence of an isotope effect in those spectra where the properties of the nucleus play an important rôle in determining the spectral terms and intensities. Consequently, since in molecular spectra the rotational and vibrational energy of the nuclei determine the fine structure and spacing of the bands as a whole, respectively, comparatively large effects may be looked for. An isotope effect due to the electronic transition may be expected to be of the same order of magnitude as in atomic spectra, and can be left out of consideration.

The theory of the isotope separations in band spectra was developed for vibration-rotation bands by Loomis (8) and Kratzer (9).

Mulliken (10) has worked out the theory of isotopic separations for electronic bands very fully, and most of the later work has been based on his paper. Further contributions have been made by Gibson (11), Patkowski and Curtis (12) and Birge (13).

Since we are concerned chiefly with intensities rather than energy separations in the isotope effect, only the results of the theory of isotopic separations will be indicated briefly. If the nuclear masses of a molecule be m_1 and m_2, the quantity $\mu = \frac{m_1 m_2}{m_1 + m_2}$ which is called the "reduced" or "effective mass", enters into the formulae for rotational and vibrational energy. If now one of the atoms of the molecule has isotopes, for the molecule containing the isotope we have a different value of the effective mass.

We may suppose that the molecule of effective mass μ is the more abundant; this will be referred to as the "main molecule", and the other molecule will be called "the isotope". The constants of the latter molecule will be indicated by the superscript i above the various symbols. If the vibrational energy levels (expressed in wave-numbers) for the main molecule be represented by

$$\nu_v = \omega_0 (v + 1/2) - b (v + 1/2)^2 \qquad (1)$$

then those for the isotope are given by

$$\nu^i_v = \varrho\, \omega_o (v + 1/2) - \varrho^2 b (v + 1/2)^2 \qquad (2)$$

where $\varrho = \sqrt{\mu/\mu^i}$.

For the rotational levels, we have for the main molecule

$$\nu_r = \mathrm{B}\, m (m + 1) + \qquad (3)$$

and for the isotope

$$\nu^i_r = \varrho^2\, \mathrm{B}\, m (m + 1) + \qquad (4)$$

The vibrational separation of the band origins is given by

$$\nu^i_v - \nu_v = (\varrho - 1)\, (\omega_o'(v' + 1/2) - \omega_o''(v'' + 1/2) \\ - (\varrho^2 - 1)\, (b'(v' + 1/2)^2 - b''(v'' + 1/2)^2) \qquad (5)$$

and the rotational separations of the lines by

$$\nu^i_r - \nu_r = (\varrho^2 - 1)\, [\mathrm{B}\, m'(m' + 1) - \mathrm{B}''\, m''(m'' + 1) +] \qquad (6)$$

It may be seen from these equations that the vibrational isotope effect causes a separation of the band origins of main molecule and isotope; the separation, at least for low values of v' and v'', increases with increasing distance from the origin of the system (i.e. the point at which the change in vibrational energy is zero). For higher values of v' and v'', this is no longer true and the individual cases must be worked out.

The rotational effect causes a similar, though generally smaller separation of the lines, also increasing with increasing distance from the band origin (i.e. the position where the change in rotational energy is zero).

When vibration and rotation states change simultaneously, as is generally the case, the separation for the isotope is of course obtained by adding the vibrational to the rotational separation. If there are more than two isotopes, then we may expect as many components of the band lines as there are isotopes.

The first evidence of the isotope effect was found by Loomis (8) and by Kratzer (9) in Ime's data on the infra-red spectrum of HCl. Then followed several investigations of Mulliken (33), (14) & (15) in which the effect was found and measured in boron, copper and silicon in the spectra of BO, CuBr. Cu Cl and SiN.

Since the discovery of the effect in these spectra, much work has been done with a view to extending our knowledge of isotopy, and important results have been obtained.

Summaries of the results achieved up to the year 1929 are to be found in refs. (16) & (17). Up to that time, only corroborations of Aston's results had been obtained, but still more recent work has resulted in the discovery of four isotopes hitherto unknown, viz. O^{17}, O^{18}, C^{13} and N^{15} existing in very small quantities relatively to the main isotope. (An isotope of chlorine (mass 39) has also been reported (see p.)

References (18) to (20) may be consulted in connection with these isotopes.

Having now briefly considered the isotope effect, we proceed to a consideration of the relative intensities of the spectral lines of isotopes.

Intensities in Isotopic Molecular Spectra.

The intensity of a spectrum line is governed by the number of emitters in the initial state, and by the probability of transition between the levels concerned.

Since the energy states of isotopic molecules never differ very greatly, it is clear that differences in intensities of isotopic lines will be chiefly due to the relative abundance of their respective molecules. It is, however, of interest to consider to what extent the mass may affect the above two factors, apart from the relative abundance of the isotopes.

Various properties of the molecule e.g. probability of excitation (under particular conditions), may be expressed as a function of the vibrational energy. These various properties will in general have different values for the same quantum state in isotopic molecules, and it is required to determine these values for the isotopes. In order to do this, we make the assumption that the various properties under consideration are the same functions of the vibrational energy for the isotopes. This is a very reasonable assumption, since the potential energy functions of isotopic molecules are almost certainly identical. The energy states which are allowed by the quantum conditions are, however, different for the isotopes, and these must be used in deriving the values of the required quantities from the relation which expresses these quantities as a function of the vibrational energy. In other words, if we plot each of the various quantities against the vibrational energy for one isotope, then the values of these quantities for other isotopes are given directly by inserting the appropriate vibrational energy values in the graph.

(a) Intensities of Bands.

We will first take the case of zero rotation, and consider vibrational transitions within an electronic band system.

Where temperature equilibrium holds, the numbers of molecules in the different levels are proportional to the Boltzmann factor $e^{-\frac{E_\nu}{kT}}$. (E_ν = vibrational energy, k = Boltzmann constant and T = the absolute temperature).

If p be the transition probability, the intensity of a band *) is

$$I = A p e^{-\frac{E_\nu}{kT}} \tag{7}$$

where A is a constant for a particular molecule, and may be

---

*) Strictly speaking, in order to derive the number of emitters from the number of molecules, the statistical weight of the levels should be considered; this is probably constant with respect to the vibrational quantum number, however, and hence does not effect our problem.

called the abundance. For two isotopic molecules, the intensity ratio is

$$\frac{I}{I^i} = \frac{A}{A^i} \frac{p}{p^i} \, e^{\frac{E^i_\nu - E_\nu}{kT}} \tag{8}$$

If E_ν is expressed in wave-numbers, the expression becomes

$$\frac{I}{I^i} = \frac{A}{A^i} \frac{p}{p^i} \, e^{\frac{E^i_\nu - E_\nu}{0.7\,T}} \tag{9}$$

In bands observed in high temperature sources, (arc bands, for example) it is unlikely that the exponential factor will ever differ appreciably from unity. In bands at low temperatures, the factor may have considerable influence on the intensity ratio, however. It does not appear to have been considered hitherto, but as the results of Chapter II show, it is not so small as might at first sight be expected.

If thermal equilibrium does not exist, then the distribution of energy states does not follow the Boltzmann law, but may be supposed to be a function of the vibrational energy; we suppose that the same function holds for different isotopes. If this is so, then

$$\frac{I}{I^i} = \frac{A}{A^i} \frac{f(E_\nu)}{f(E^i_\nu)} \tag{10}$$

Whether the value of $\frac{f(E_\nu)}{f(E^i_\nu)}$ differs appreciably from unity depends upon the form of the function, and on the values of E_ν and E^i_ν. Particularly in the case of excitation by active nitrogen, it appears that this factor may have a decided influence on the intensity ratio, and the results on the intensity ratio of the isotopes in the spectrum of BO, (chap. IV), may be consulted in support of this.

The possibility of p depending on the nuclear mass must nom be considered. At first sight this does not appear probable, but it must be remembered that the transition probability is a function of the energy of the levels involved.

We may consider an actual case, in which the intensities for a v'' progression (i.e. with v' constant) are plotted against v'' *(fig.* (6), *p.* 48.

In general, as predicted by Condon's theory (21), we should expect two maximum values of the intensity; since all transitions are from the same level, the ordinates are proportional to the transition probabilities *p*. We may again assume that this curve would be the same for both isotopes if they both had identical upper levels. The values of *p* would then be given by the ordinates at the appropriate values of the vibrational energy, as shown by the full and dotted vertical lines, representing existing states of the two isotopes. It is evident that at large values of v'' and when on a steep part of the curve, the values of *p* for the isotopes may differ appreciably. We have, however, assumed that the two isotopes have identical upper states, but these differ also. If we can draw a whole "familly" of transition probability curves, one for each of the various upper states for one isotope, we can form an idea of how the curve depends on the vibrational energy in the upper state. Again assuming that the transition probabilities are the same functions of the two isotopes (but that the energies of existing states are different) we can insert the appropriate energy values and so arrive at the curves giving the transition probabilities from each of the upper states to the various lower states, for the other isotope. Inserting in these curves the appropriate energy values, we obtain the transition probabilities for the isotope. Whether the values of *p* differ appreciably for the two isotopes depends on the energy separation and on the form of the p-E_v curves, and it is impossible to draw general conclusions. An example is provided in chap. IV where the case of the BO bands is worked out. The experimental results, however, do not support the above theory, as will appear later.

(b) Intensities of Rotation Lines.

With regard to the distribution of the molecules over different rotation states, the same considerations apply here as in the vibrational energy states, and the different energies of two isotopes will cause a difference in concentration, this being again given (when temperature equilibrium holds) by the Boltzmann factor (see equation (7). Here, however, the energy differences are in general smaller than those for vibrational energy, and the effect is probably always negligible. When temperature equilibrium does not hold, a small difference may be expected, but this is not likely to be appreciable. The bands of boron monoxide, where the energy differences for the two isotopes are relatively great, should provide a suitable case for revealing the effect, if it exists, but as will be shown in chap. IV, no such effect has been found.

The transition probabilities for a particular rotational transition are proportional to the larger of the two rotation quantum numbers involved (22), consequently no difference for the two isotopes is to be expected.

From the foregoing, it will be seen that the measurement of the intensity ratios of isotopic bands may be expected to give a reliable and exact value of the relative abundance of isotopes, when the necessary corrections are applied. It seemed, however highly desirable to test the method first on elements where only two isotopes exist in appreciable quantity, so that a comparison with the isotope ratio calculated from the atomic weight might be made. Measurements were first made on the absorption band spectrum of chlorine, but that spectrum is too complicated to be suited for exact intensity measurements, and further measurements on the spectrum of boron monoxide were made. These experiments will now be described.

CHAPTER II.

The isotope effect in the band spectrum of Chlorine, and the determination of the nuclear spin of Cl^{35}.

Chlorine, like its related elements bromine and iodine, possesses an absorption spectrum which is characterized by many thousands of lines grouped into bands, followed on the short wave-length side by a wide region of continuous absorption. The vibrational structure has been analysed by Kuhn (23) and Nakamura (24).

The bands consist of P and R branches, as was shown by the rotational analysis carried out by the writer (25), and have generally been attributed to a $^1\Sigma \leftarrow {}^1\Sigma$ transition. Recently, however, Mulliken (26) has pointed out that the upper state cannot be $^1\Sigma$, and that the transition involved is probably $^3\Pi \leftarrow {}^1\Sigma$.

Since chlorine has isotopes 35 and 37 (1), three molecules must exist viz. $Cl^{35\text{-}35}$, $Cl^{35\text{-}37}$, and $Cl^{37\text{-}37}$. In his earlier work on the chlorine isotopes, Aston (1) found a faint line in the position corresponding to mass 39. Later investigations made him consider that this could not be ascribed to chlorine, and that an isotope Cl^{39} could not be present in appreciable quantity. Recently, however, Becker (27) has found a third component of the band lines of the vibration-rotation band of HCl, and this is ascribed to an isotope of chlorine, of mass 39. Should this be correct, the relative abundances given below may require a small correction; the isotope Cl^{39} can only be present in very small quantities, however, and can hardly affect the figures seriously.

Taking the atomic weight of chlorine as 35.457 and the masses of the chlorine atoms (correcting for O^{17} and O^{18}) as 34.980 and 36.976, the ratio $Cl^{35} : Cl^{37}$ is 3.185 : 1. The molecules $Cl^{35\text{-}35}$, $Cl^{35\text{-}37}$, and $Cl^{37\text{-}37}$ must therefore occur in the proportions 10.144 : 6.370 : 1 respectively. The vibrational isotope effect in this case will cause a tripling of all the bands in the system, the separations being given by inserting the appropriate value of the coefficient ϱ in equation (5) p. (12). For the two molecules $Cl^{35\text{-}35}$, and $Cl^{35\text{-}37}$, ϱ has the value 0.9863.

The bands due to $Cl^{35\text{-}35}$, which are the strongest, are easily observed, and have been analysed for the 1-11, 1-12, 1-13, 2-6, 2-7, 2-8 and 2,12 vibrational transitions (25). These bands show the phenomenon of alternating intensities, as is to be expected in a molecule with equal nuclei (28) and (29).

In the case of the 1-12, 2-6 and 2-12 bands, the weaker bands due to the molecule $Cl^{35\text{-}37}$ have been identified and measured; here the nuclei are no longer identical, and no alternation in intensity results, again in accordance with theory. A search for the bands of $Cl^{37\text{-}37}$ (which must be very weak) was made, but without success. It would be of very great interest to carry out intensity measurements in these bands, since alternating intensities are again to be expected here. The measurement of the alternating intensity ratio enables the nuclear spin to be determined, and if it could be carried out for the two symmetrical chlorine molecules, a comparison of nuclear spins for the isotopes could be made. The complication of the spectrum has hitherto prevented this from being done, however, and the nuclear spin has only been determined for the more abundant isotope. The determination of this quantity, and of the intensity ratio of the molecules $Cl^{35\text{-}35}$ and $Cl^{35\text{-}37}$ will now be described.

Intensity Measurements.

The chlorine absorption bands were photographed in the first and second orders of a 6m. grating, with an absorbing column up to 9m. in length. As a continuous source, the positive pole of a carbon arc was employed.

In all the intensity measurements, the usual method employed at Utrecht (30) has been used, and from the photographic densities (measured from the microphotometer record), the corresponding intensities were found from a calibration curve. The latter was obtained from a plate developed simultaneously with the chlorine plate, on which spectra of a tungsten lamp were photographed; the intensity of these spectra was varied in a known manner by means of "step reducers", and the densities corresponding to these intensities (at the required wave-length) were measured. From these, a density-intensity curve was drawn, one for each band; this was desirable since the form of the calibration curve alters somewhat with wave-length, though within one band it was sufficiently constant. The absorption coefficients for the centres of the lines were then calculated.

The intensity of an absorption line is measured by the value of $\int_{-\infty}^{+\infty} a_\nu \, d\nu$ where a_ν is the absorption coefficient for the frequency ν in the usual absorption formula $I = I_0 \, e^{-a \varrho x}$ and the determination of the absolute intensities would involve the integration of a_ν over the whole breadth of the line, for every line. Since the determination of the absolute intensities was not the chief object of this work, the integration has not been carried out for these lines, and the maximum value of a_ν i.e. the coefficient of absorption for the centre of the line, has been determined.

If all the lines measured were of the same shape, then it is clear that the ratio of intensities of two lines 1 and 2 would be given equally well by the ratio $\int_{-\infty}^{+\infty} a_{\nu_1} \, d\nu \Big/ \int_{-\infty}^{+\infty} a_{\nu_2} \, d\nu$ or by $a_{(max)1} / a_{(max)2}$ and no error could be introduced by employing the latter. There is no reason for thinking that the shape of single band lines will alter, at least within one band, and the different shapes of the lines which appear on the photometer curves must be chiefly due to blending with other lines. Now the integrated absorption coefficient would be at least as much in error as the central absorption coefficients on this account, and might conceivably be even more disturbed than the latter, which has consequently been employed as a measure of the intensity.

In all absorption measurements, the finite resolution of the spectrograph and the width of the slit cause the absorption lines to appear less deep than they are in reality. So far as relative measurements are concerned, this would not matter if all the lines were of the same shape, but the lines as actually observed differ somewhat in this respect.

To determine the correction for each line would have necessitated very great labour, but the influence on the intensity relations could be investigated as follows. The band 1 → 12 (which on account of its strength could be observed with a single tube and consequently did not require very long exposures) was photographed in the first order with the slit width employed throughout this work (namely 0.02 mm.) and also with a slit width 0.04 mm., and in the second order with slits of 0.03 and 0.04 mm. The intensities of seven of the narrowest lines were then measuered from these four plates. Although the absolute intensities varied considerably, the values of the intensity ratio for strong and weak lines only differed from the mean by -4.5, 0, -2, and 1% for the slit widths 0.04 mm. (first order), 0.02 mm. (second order), 0.04 mm. (second order), and 0.03 mm. (second order). These results indicate that the true ratio may perhaps be somewhat larger than the measured one, but it is also possible that the differences are accidental. Since the lines on which these test measurements were made are narrower than most of the lines whose intensities have been measured, the effect (if real) will in general be smaller than that above, and has been neglected in the final result for the intensity ratio.

The differences in the absolute absorption coefficients are irregular and much greater, being even as large as 100%. This is not in the direction which would be expected if it were due to the finite resolution of the spectroscope, and is probably due to developer effects, which are known to occur when there is a steep density gradient on a photographic plate, as in narrow absorption lines.

Alternating Intensity Ratio.

The average value of the lines in one branch having odd J — values has been compared with that of the even J lines in the same branch, for the 1 → 11, 1 → 12, 1 → 13, 2 → 7, 2 → 8, and 2 → 12 bands. This is equivalent to finding the ratio of intensity of a strong line to that of the mean of the two adjacent lines; since the intensity of the chlorine band lines does not vary quickly with J, this procedure does not introduce any appreciable error. The results are given in Table I. The mean of the ratio for the P and R branches for each band is fairly consistent. A weighted mean value for all the bands has been taken, in which the value for each band has been weighted according to its closeness to the mean. This final value for the ratio of the alternating intensities (1.36 : 1), has been derived from more than 170 lines, and may therefore be considered fairly reliable; the mean error calculated from the divergence of the individual values for each band from the mean is 0.057.

By taking an average over a very large number of lines in this way, one can to a considerable extent get rid of the errors due to blending i.e. to the fact that the lines are overlaid by other lines. But even if a sufficient number of lines has been taken to ensure that, on the average, the same intensity of overlying lines has been added to both strong and weak lines, the measured ratio of these latter will still be in error, and will be smaller than the true ratio by an unknown amount. Consequently the figure 1.36 must be regarded as a lower limit. It appears exceedingly probable that the true ratio is not greatly in excess of this, since even if the average intensity of the overlying lines amounted to 20% of the intensity of the weaker lines, the ratio would then only be raised to 1.45 : 1, and this estimate of the intensity of the overlying lines is probably too high. In view of these considerations, it is likely that the true ratio is very close to 1.4 : 1, which is the theoretical one corresponding to a nuclear spin of 5/2, and the latter is therefore taken as the most probable value for this quantity. The fact that an odd number of units of spin is found is in agreement with the fact that Cl^{35-35} has an odd number of nuclear particles (18 + 35).

Table I — Intensity Ratios.

(a) Alternating Intensities (ratio of intensity of strong to weak lines in $Cl^{35\cdot35}$).

Band	P branch	R branch	Mean
1—11	1.28	1.22	1.25
1—12	1.40 (superposed P & R)		1.40
1—13	1.43	1.34	1.38
2— 7	1.49	1.21	1.35
2— 8	1.62	1.18	1.40
2—12	1.34 (superposed P & R)		1.34

Weighted Mean 1.36

(b) Isotopes (ratio of intensity and abundance of Cl^{35-35} to Cl^{35-37}).

Band	Intensity Ratio	Relative Abundance*
1—12	1.35	1.42
2— 6	1.28	1.40
2—12	1.42	1.56

Mean 1.46

* Corrected for Boltzmann Factor.

Relative abundance of isotopes.

The intensities of Cl$^{35\text{-}35}$ and Cl$^{35\text{-}37}$ have been compared by taking the average ratio (over the lines having the same J-values) for the bands 1—12, 2—6 and 2—12 (see Table I).

In order now to arrive at the real relative abundance of the two molecules, we must first correct for the effect of the Boltzmann factor. Inserting the appropriate quantities in equn. (8) p. (5) for the initial states of the bands, we find the values of $e^{\cdot\frac{E_v^i-E_v}{kT}}$ by which the intensity ratios must be divided in order to find the real abundance ratio of the molecules. As Table I shows, this is an important correction to the ratio, amounting in the case of the vibration state $v'' = 2$ to 9%.

In order to determine the correction due to the difference in transition probability for the two isotopes, extensive intensity measurements of the bands would be necessary. It can be said, however, that the correction on this account is likely to be very small, since the intensity of the bands in a progression does not vary quickly with vibrational quantum number; this is revealed by an inspection of the spectrum. We may therefore take the average abundance ratio for the three bands viz. 1.46. This is again a lower limit. The same assumption as to the amount of overlying lines would raise the figure to 1.58. This is in excellent agreement with the value calculated from the atomic weight viz. 1.59. The experimental error, as evidenced by the deviations of the values for the three bands, is however rather great, and the assumed 20% for the overlying lines quite arbitrary. It is difficult to assess the magnitude of the probable error, but it must be certainly less than 20%.

No evidence is found of a disagreement between the abundance ratio of the isotopes determined by band spectrum measurements and calculated from the atomic weight, provided that the former is corrected for the effect of the different energies of the isotopes on the Boltzmann factor. The suggestion, made by the writer in (25) b, that the molecule Cl$^{35\text{-}37}$ had a greater absorption coefficient than Cl$^{35\text{-}35}$ on account of its asymmetry (see (18) c,), is consequently not supported by the interpretation here given.

CHAPTER III.

The Spectrum of Boron Monoxide.

Description of the Spectrum.

Two molecular spectra of boron are known, both of which are attributed to the oxides. The one consists of diffuse, headless bands, which even under high dispersion show no structure; it is emitted by a bunsen flame or a carbon arc supplied with boric acid, and is usually attributed to the molecule B_2O_3. The writer has also observed it very strongly developed in a discharge tube containing boron trichloride with an excess of oxygen, with an uncondensed discharge.

The other spectrum consists of bands which have the structure found in diatomic molecules, and was probably first observed by Ciamiacian in the spark spectrum of boron fluoride. It also occurs in the arc with boric acid on the poles, and has been observed by Hagenbach and Konen, and Kuhne (see references (32)—(35) for literature).

A further source of the bands was discovered in 1913 by Lord Rayleigh, who observed that a greenish blue colour is developed when the vapour of boron trichloride is led into active nitrogen. The spectrum was examined by Jevons (32), who measured the wave-lengths of the band heads, and showed that they form two systems, extending from 3373 Å.U. to 6371 Å.U., and from 2141 Å.U. to 3496 Å.U., which he designated α and β respectively. The α system consists of bands of complicated structure, with double-double heads, though the structure of the system itself is fairly simple. In the β system, the reverse is the case, and the bands are single-headed, but form a rather complicated system. In addition to the main bands of this latter system, he found two weaker systems, which he designated β_1 and β_2 respectively. As he remarks, these subsidiary systems are not entirely independant of the main β system, since the heads are single, and the intervals and second differences are of the same order of magnitude.

The spectrum was further investigated in 1925 by Mulliken

(33) in connection with a search for evidence of the isotope effect in band spectra, and he was able to show that the subsidiary systems were due to the less abundant isotope of boron (B^{10}). The complete systems due to this isotope were identified and measured, and it was shown that the magnitude of the isotopic separation could only be accounted for by assuming that the emitter of the spectrum was BO, and not BN as Jevons had concluded from chemical evidence. In addition to the α and β systems (which have a common final level), Mulliken found a much weaker intercombination system, in which the initial state is identical with the initial state of the β system, while the final state is identical with the initial state of the α bands.

The α bands have been photographed under high dispersion and analysed by Jenkins (34), using the active nitrogen source, and Mulliken's classification of these bands as $^2\Pi \rightarrow {}^2\Sigma$ (33) was confirmed, but the doubling of the $^2\Sigma$ level could not be detected. The existance of a vibrational isotope displacement for the 0—0 band provided very definite evidence for the vibrational half-integral quantum numbers required by the quantum mechanics; this had already been indicated by Mulliken's equations for the isotopic displacement. The rotational isotope effect was examined, and the nuclear separation was found to be identical for both isotopes.

A number of the bands of the same system developed in the arc have recently been analysed by Scheib (35), who finds the same structure as Jenkins, and also failed to find a doubling of the $^2\Sigma$ level.

The two methods of excitation give spectra of very different appearance. In the arc, the rotation structure is greatly developed, and the band heads difficult to distinquish, whereas in the active nitrogen source, the heads are very prominent.

In the β system, there appears at first sight to be only one branch present in most of the bands, as in general only one series of lines is associated with each head. Mulliken (33) first interpreted this as a single R branch, and considered that the P branch was missing. The writer (36) was also of the same opinion, but understands from Mr. A. Harvey that Prof. Mulliken has come to the conclusion that both P and R branches are present in the bands excited by active nitrogen and in the arc. The R branch forms the head, and on account of the low temperature it fades out soon after having turned back upon itself at the head. Since the lines in the neighbourhood are closely spaced and are not resolved with the spectrographs used, the lines of the R branch are not observed as lines. The P lines, however, do not form, the head of the band, and not being crowded together like the R lines, are observed as a series of lines. The net result is that the bands consist of a strongly developed head and a single series of lines viz. the P branch.

This explanation of the apparently missing branch seemed very probable, and the frequencies of the lines in the 0—2 band excited by active nitrogen were measured. These, when compared with the lines of the same band in the arc (see Table IV) show clearly that the lines in the band excited by active nitrogen form the P branch. It is, therefore, almost certain that the R branch is contained in the head, and that P and R branches occur in both sources.

In the α bands, the same structure has been found for arc and active nitrogen sources (34) and (35), and we may suppose that the differences in both systems which result from the two modes of excitation are (at least for a great part) due to the difference of temperature of the sources. The much higher temperature of the arc causes the maximum of intensity to lie at higher rotation levels than in the active nitrogen source, and gives a much greater developement of the rotation structure. In the β bands in the arc, the R branch is so far developed that it extends far past the head, and may be observed as a series of lines lying amongst the P lines.

Boron is a particularly favourable element for the study of the isotope effect; it is light (atomic weight 10.82), and consequently the difference in mass of the two isotopes is a considerable fraction of the mass of either. Further, the relative abundance is not high; taking the masses of the atoms as 11.0110 and 10.0135 (37), or, correcting for O^{17} and O^{18} (^{20}c) as 11.0096 and 10.0122, the relative abundance for the above atomic weight is 4.22 : 1 or 4.26 : 1 respectively.

For the boron monoxide molecule, the isotope coefficient ($\varrho-1$) (see equation (5) p. (12) is high viz. 0.0292, and the isotopic separation of the band lines is in consequence great compared with that in most spectra where isotopes are present. Further, the spectrum is not unduly complicated, particularly in the β system excited in active nitrogen, nor is the band structure too fine for resolution with spectrographs of moderate dispersion, except quite near the heads.

Experimental.

During the course of the investigation on the intensity ratios of the isotope bands in boron monoxide, the author was led to examine the β bands in the arc. A Hilger E1 quartz spectrograph was used to photograph the region 2400—2600 Å.U., where the dispersion is about 3 Å.U. per mm.; a reproduction of the bands in this region, taken with an exposure of four minutes, is shown in Plate (I). A narrow slit was used, and since no appreciable temperature shift could occur in the short exposure time, the maximum resolution was obtained.

The doublets in the bands of $B^{11}O$ mentioned by Mulliken (33) were examined, and it was found that at some distance from the head, each member of a doublet was itself double, the separation being, however, greater for the series of lines which appears also in bands excited by active nitrogen. The (fine) doublet separation increases with distance from the band head, and resolution begins at about the thirty-sixth and forty-fifth lines from the head in the wider and narrower series of doublets, respectively.

The frequencies of the lines in the 0—1 and 0—2 bands were measured, using iron arc lines as standards. In these measurements, the lines from the twentieth to the fiftieth from the head have been measured, and since the determination of the fine doublet separation was not the immediate object of the work, the mean frequency of these doublets has been determined.

Analysis.

The appearance of the arc β bands described above is just what would be expected for a ${}^2\Sigma \rightarrow {}^2\Sigma$ transition with all the branches present. Bands of this type have a P and an R branch, each of them consisting of doublets whose separation increases linearly with the rotation quantum number; a consequence of the connection between these latter is that, when the R branch forms the head and the doublets become resolved after this branch has turned at the head, the R lines are resolved nearer the origin than the P lines. Since the two bands measured have a common initial level, identical combination differences of the type $R(m) - P(m) = \Delta_2 F'$, where m is the effective quantum number in the lowest electronic level, should be found if the two series of fine doublets are P and R branches (neglecting the fine doubling).

Two such sets of combination differences have in fact been found and are given in the second and third columns of Table II. The agreement is good enough make it exceedingly probable that they are genuine $\Delta_2 F'$ values. A further test can, however, be applied, since the α and β system have a common final level, and the $\Delta_2 F''$ values must therefore be identical for bands which have the same vibrational quantum number in the final state in the two systems. For the β bands, the values of $\Delta_2 F'' = R(m-1) - P(m+1)$ can readily be calculated from the line frequencies after the $\Delta_2 F'$ s have been determined. For the α bands, Scheib gives the same combination differences for the 0—2 and 0—3 bands from his analysis; in columns (6) and (7) of Table II these differences for the 0—2 band in both systems are reproduced. The agreement is such that there can be no doubt that the $\Delta_2 F''$ s for the β band are genuine. We may therefore conclude without hesitation that the two series of fine doublets are P and R branches, and that the bands have the structure of ${}^2\Sigma - {}^2\Sigma$ bands.

Determination of Rotation Constants.

The rotation term for $^2\Sigma \rightarrow {}^2\Sigma$ bands (neglecting the fine doublet structure) may be represented by

$$F = B\,m\,(m+1) + D\,(m\,(m+1))^2 \qquad (11)$$

where *m* is the "effective" rotation quantum number. The combination differences for the upper and lower states are then respectively

$$\Delta_2 F' = R(m) - P(m) = 4\,B'\,(m + {}^1/_2) + 8\,D'(m + {}^1/_2)^3 \qquad (12)$$

and

$$\Delta_2 F'' = R(m-1) - P\,(m+1) = 4\,B''\,(m + {}^1/_2) + 8\,D''(m + {}^1/_2)^3 \quad (13)$$

The values of *m* were determined by plotting $\Delta_2 F'$ (mean values of 0—1 and 0—2 bands) against an arbitrary series of consecutive whole numbers, and extrapolating the curve (which shows a slight departure from linearity) to $\Delta_2 F' = 0$. Since at this point $m = -\,{}^1\!/_2$, the absolute values of *m* may be determined from the curve (fig. (1)).

It is found that integral values of *m* are required in equation (11). After the determination of the *m*-values for the Δ_2 F's for the upper state, those for the lines can be found at once.

The value of B is in first approximation one-quarter of the slope of the $\Delta_2 F$-*m* curve. The values so obtained (for both upper and lower states) may be substituted in equations (12) and (13) and the values of D determined. This serves to determine D sufficiently accurately. Then B may be re-calculated, using equations (12) and (13) with the known value of D.

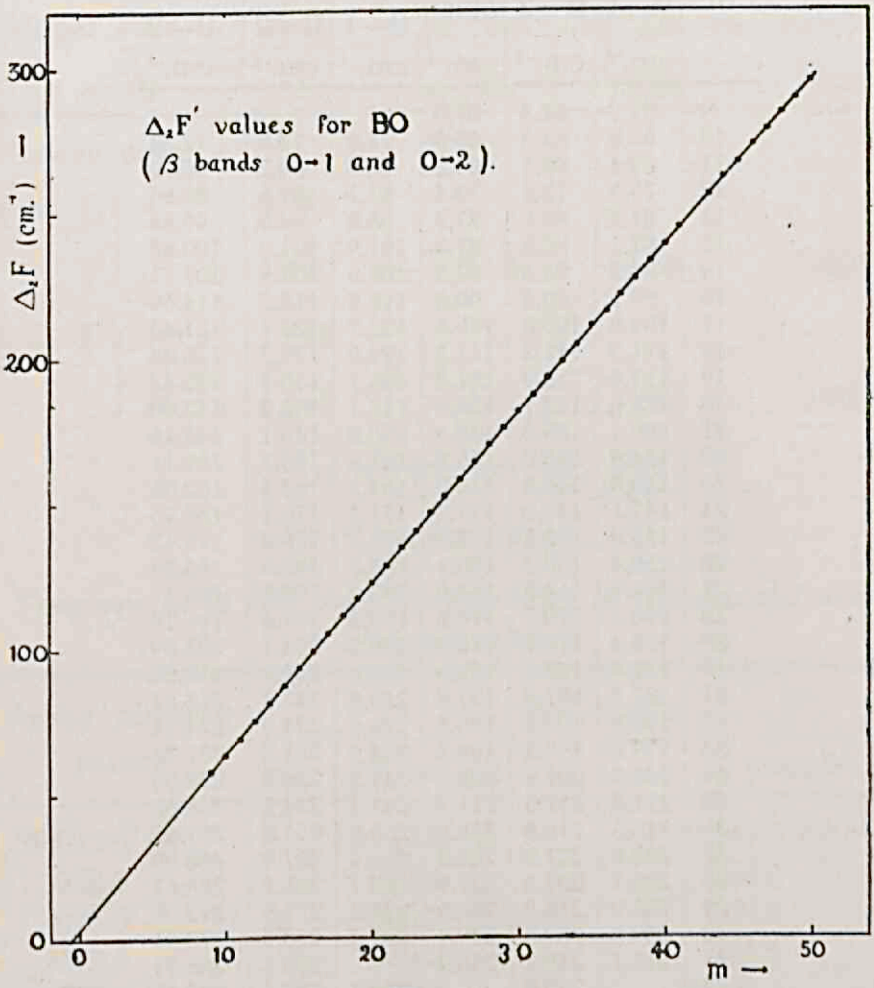

Fig. 1.

In this way, the values of B and D for both states have been determined; the average values over the range $m = 10$ to $m = 50$ are given in Table III. The excellent agreement of the B'' values with those of Scheib may be pointed out. The moments of inertia and half-internuclear distances of the BO molecule have been calculated from the B's and are given in the same table.

Table II.

Combination Differences for Upper and Lower States in BO.

m	Δ_2F'			Δ_2F''		
				β bands		α bands*
	0—1	0—2	Mean	0—1	0—2	0—2
	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
9	57,7	57.3	57.5			
10	63.8	63.3	63.5	73.9	72.8	72.84
11	69.4	69.1	69.2	80.8	80.2	80.00
12	75.5	75.4	75.4	87.7	87.5	86.64
13	81.2	81.6	81.4	95.0	94.0	93.84
14	87.1	87.5	87.3	101.9	101.0	100.62
15	93.2	93.8	93.5	108.6	107.9	107.71
16	99.1	99.5	99.3	115.5	115.2	114.59
17	104.9	105.8	105.4	122.7	122.1	121.43
18	111.3	111.3	111.3	129.5	129.2	128.34
19	117.4	116.9	117.2	136.7	135.4	135.42
20	123.0	122.7	122.9	144.1	142.2	142.00
21	129.1	128.8	128.9	150.8	149.1	149.16
22	134.9	135.0	135.9	157.6	155.7	156.11
23	140,9	140.8	140.0	164.7	163.4	162.95
24	147.1	147.0	147.3	171.7	170.1	169.75
25	152,9	152.5	152.7	178.7	176.8	176.42
26	158.4	158.4	158.4	185.7	183.6	183.38
27	164.4	164.8	164.6	192.2	190.5	190.47
28	170.3	170.7	170.5	199.3	197.4	196.79
29	176.4	176.1	176.3	206.2	204.7	203.89
30	181.9	182.1	182.0	213.0	211.1	210.84
31	187.7	187.9	187.8	219.8	217.7	217.67
32	193.8	193.8	193.8	226.6	224.9	224.34
33	199.3	199.2	199.3	233.9	231.5	231.23
34	205.3	204.9	205.1	241.2	238.0	238.00
35	211.8	211.5	211.7	247.4	244.7	244.86
36	216,6	216.6	216.6	253.9	251.8	251.57
37	222.5	221.9	222.2	260.6	257.9	258.90
38	228.1	227.8	227.9	268.1	265.1	265.67
39	233.9	233.9	233.9	274.3	271.9	272.05
40	239,5	239.3	239.4	281.3	278.2	279.01
41	245.1	245.2	245.2		285.2	285.71
42		250.8		294.4	292.3	292.15
43	256,3	256.7	256.5	301.5	298.5	298.89
44	262,3	262.1	262.2	308.0	305.2	305.13
45	267.6	267.7	267.6	315.2	311.9	312.34
46	273,5	273.3	273.4	321.3	318.8	318.92
47	278.7	279.0	278.9	328.5	325.0	325.24
48	284.8	284.5	284.7	334.6	331.7	331.63
49	289.4	289.7	289.6	341.6	338.6	338.17
50	295.3	295.6	295.5		345.6	345.13
51					351.8	351.23
52					357.5	358.08
53					364.8	364.68

* See ref. (35).

Table III.

Rotation Constants of $B^{11}O$ *(β system).*

	B	D	I	r
Upper state	cm.$^{-1}$	x 10^{-5} cm.$^{-1}$	x 10^{-40} gm. cm.^{2}	x 10^{-8} cm.
($v = 0$)	1.512	— 1.05	18.26	0.649
Lower state				
$v = 1$ α*	1.761			
β	1.760	— 0.75	15.69	0.6016
$v = 2$ α*	1.745			
β	1.745	— 0.8	15.82	0.6041

* α system; see ref. (35).

Table IV.

Frequencies of BO *lines in* 0—2 *band in the arc and active nitrogen source.*

Active nitrogen source	Arc source	
	P branch	R branch
39,049.6 cm.$^{-1}$	39,048.9 cm.$^{-1}$	39,044.7 cm.$^{-1}$
038.1	037.4	033.2
026.0	025.5	020.8
013.8	013.2	007.5
000.4	000.3	38.994.3
38,987.3	38,987.0	981.0
973.2	973.3	966.2
959.2	958.6	951.2

CHAPTER IV.

The Relative Abundance of the Isotopes of Boron, as determined by Intensity Measurements.

Apparatus and Methods.

As has been stated in chap. III, two methods of exciting the spectrum of boron monoxide are available viz, the arc with boric oxide on the poles, and active nitrogen (containing a trace of oxygen) into which the vapour of boron trichloride is led. The former method involves the use of a much higher temperature than the latter, and as is to be expected, gives a greater developement of the rotation structure. In consequence, the spectrum as excited by the latter source is much simpler, and the isotopic lines can be more readily distinguished; their intensities are also very much less subject to disturbance on account of superposition of structure lines of other bands.

These considerations led to the choice of the active nitrogen for exciting the boron monoxide bands for a measurement of the isotope ratio. The method has been described by Strutt (31), Jevons (32), Mulliken (14), and Jenkins (38), but for convenience will be again briefly described.

Apparatus.

The apparatus is shown schematically in fig (2). Commercial nitrogen from a cylinder (connected with the flasks F_1 and F_2 which acted as a reservoir and safety device) was passed successively over two tubes containing moist phosphorous by which most of the oxygen was removed. The nitrogen was then partly dried by contact with calcium chloride, passed over sodium hydroxide to remove any carbon dioxide, and further dried with phosphorous pentoxide.

The tubes were 1 m. long and 3 cm. in diameter, with the exception of the P_2O_5 tube, which was 60 cm. × 1 cm.

It was found that the nitrogen contained phosphorous vapour, which attacked the tap-grease of the discharge tube during long exposures, and a liquid-air trap L_1 was inserted between the last drying-tube and the discharge tube; this device lessened the difficulty considerably. The nitrogen entered the discharge-tube A, where a powerful condensed discharge was passed between two nickel electrodes 10 cm. apart. It was found necessary to make the tube of hard (suprax) glass, as the heating was considerable. The diameter of the tube was 1.5 cm., a wider tube having proved less succesful. The discharge was provided by an induction coil, with 6 amp. in the primary, in which circuit was inserted a mercury break. The terminals of the secondary were connected to the coatings of two large Leyden jars (the latter were in parallel) and through a spark-gap of about 0.5 mm. to the dicharge tube.

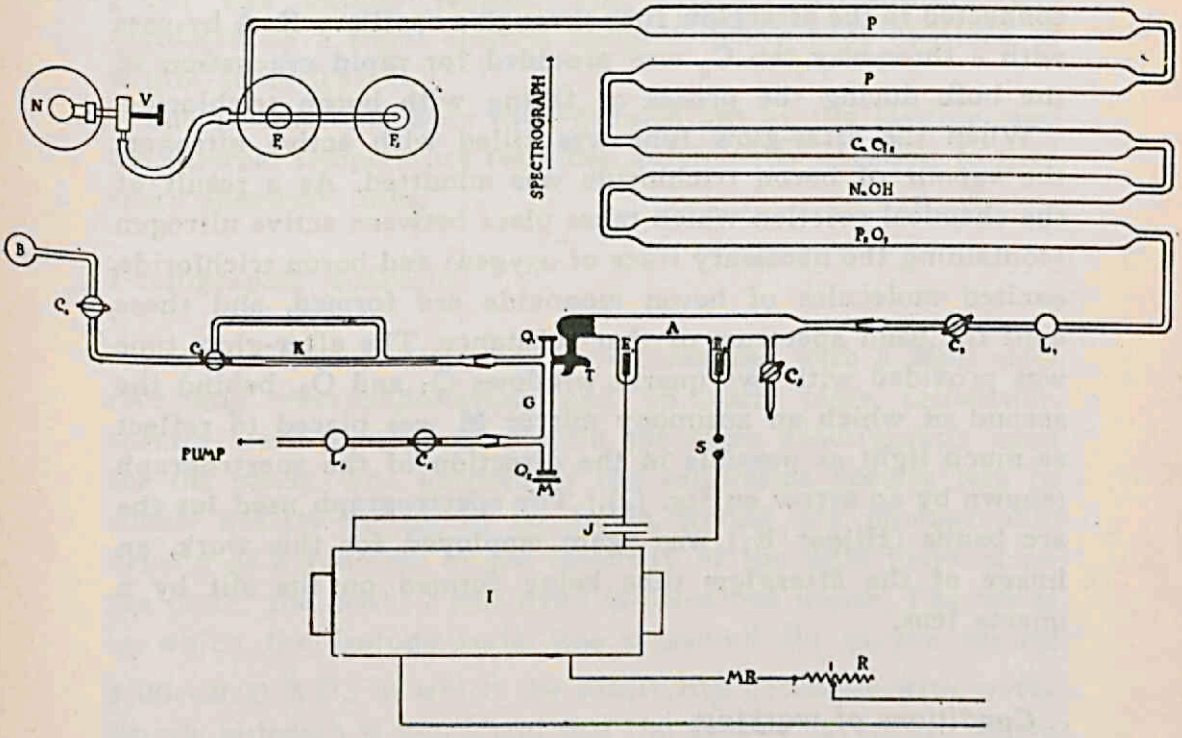

Fig (2) — Diagram of Apparatus.

With this arrangement, the nitrogen was activated and passed through a black-painted light-trap T to the after-glow tube G (of 0.8 cm. diam.) and thence through a second liquid air trap L_2 to the pump.

A fairly high pressure was mainained in the discharge tube; usually the discharge was of the forked type which occurs at a pressure of several centimeters.

The boron trichloride (supplied by Kahlbaum and stated to be prepared from Chilian boron) was contained in the bulb B, connected to the afterglow tube through a capillary K. A by-pass with a three-way tap C_3 was provided for rapid evacuation of the bulb during the proces of filling with boron trichloride.

When the after-glow tube was filled with active nitrogen, the vapour of boron trichloride was admitted. As a result of the chemical reaction which takes place between active nitrogen (containing the necessary trace of oxygen) and boron trichloride, excited molecules of boron monoxide are formed, and these emit the band spectrum of that substance. The after-glow tube was provided with two quartz windows Q_1 and Q_2, behind the second of which an antimony mirror M was placed to reflect as much light as possible in the direction of the spectrograph (shown by an arrow on fig. (2).) The spectrograph used for the arc bands (Hilger E_1) was again employed for this work, an image of the afterglow tube being formed on the slit by a quartz lens.

Conditions of working.

With the amount of phosphorous used, it was found that too much oxygen was removed for maximum brightness of the bands, and for some of the exposures, a little air was admitted through the stopcock C_5: Mulliken (33) describes a similar phenomenon. It was found, however, that with the oxygen content adjusted for maximum brightness, the beta bands of nitric oxide were strongly developed. In later work, the tap C_5 was always kept closed, and the gas velocity (on which depends the amount of oxygen removed) adjusted so that there always remained a trace of the yellow glow of active nitrogen in the tube between L and G. Under these conditions, most of the nitric oxide bands disappeared; the 2—7 band of BO was however never quite free from a strong neighbouring NO band.

The strong BO bands 2—5 and 2—6 were obtained with exposures of three hours, but for other bands, exposures up to twelve hours were necessary. It was, of course, necessary to keep the temperature constant during the exposures, and the spectrograph was heavily lagged. The external temperature was regulated by a small electric radiator, being kept constant to within about 0.5° C.

The fluctuations were then damped out by the lagging, and the internal temperature remained sufficiently constant to give sharp spectrum lines.

Photographic technique.

The densities of the lines were measured with a Moll self-recording microphotometer, and on each plate, calibration spectra were photographed with the same spectrograph used for the bands. The purpose of the calibration spectra was to enable density curves to be drawn, giving the photographic density as a function of the intensity of the light incident on the plate; the method employed is described below. The bands in which the isotope ratio was measured lie in the region 3100—2600 Å.U., in which the sensitivity decreases with wavelength, although it was found that the density curves are nearly parallel throughout this range. The variation is, however, gradual, and since the isotope separation is of the order 20 Å.U., it was possible to read off the intensities of both isotopes from one density curve, and then apply a correction to the intensity ratio on account of the change in plate sensitivity. The latter quantity was determined by using a lamp in which the energy distribution was known (see below).

In the earlier experiments, Ilford Iso-Zenith plates were used, but the grain was found to be somewhat coarse. The effect of this was minimised be photometring each spectrum line three times (at different heights) and averaging the intensities. The labour involved was very considerable, however, and experiment showed that the Special Rapid plates of the same firm were equally sensitive in the spectral region used, and the grain was much finer. Still later, the photometer was arranged so that a spectrum line of about 3 mm. length could be photometred (previously only about O.8 mm. was used), and the effect of the grain was in this way automatically averaged out. The very satisfactory nature of the registration may be seen from Plate I, in which very little irregularity due to grain may be seen.

Rodinal was used as developer, and the developement was carried out until a slight fog appeared on the plate.

Calibration of the plate for determination of the intensity ratio of the isotopes.

The relation between photographic density and light intensity was determined from six calibration spectra photographed on the same plate as the boron monoxide bands, the intensity in these spectra being varied in known steps.

The calibration spectra were taken with a gas-filled tungsten band lamp, of quartz, which gave a continuous spectrum strong enough for the purpose as far as 2400 Å.U. The intensity was altered by using different slit-widths on the spectrograph, the intensity being proportional to the slit-width provided that the latter is not so fine that diffraction effects are prominent.

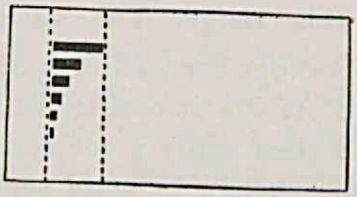

Fig. (3) — Step-Slit.

Since the exposure for the band lines was some hours, it was desirable that the time of exposure for the calibration spectra should not be too short, and the lamp current was adjusted to give a suitable density with an exposure of half-an-hour. Since it would have required much time to take the necessary sets of calibration spectra in the usual way, a "step-slit" was devised.

This consisted of six short slits of different widths, ranging from 0.07 mm. to 1.9 mm., one above the other, as shown in fig. (3). It was made by making six fine, horizontal cuts in a brass plate of 1 mm. thickness with a circular saw. Tinfoil was then pasted over the cuts, leaving, however, different lengths uncovered; these formed the slits. The slit of the spectrograph was opened as wide as possible (shown by the dotted line in fig. (3), and the step slit mounted immediately in front of, and as close as possible to the former slit. It was of course necessary to arrange that the light falling on the prism did not fill it, otherwise some of the light from the end slits would not have been transmitted, and the intensities on the plate would not have been proportional to the slit-widths. This was accomplished by two arrangements.

(a) For the region 2700—3000 Å.U., where the radiation from the lamp was rather strong, the lamp was placed at a distance of about 2½ metres from the slit in order to illuminate it uniformally. Then a quartz lens of suitable focal length was placed immediately in front of the slit, forming an image of the lamp filament on the prism. By screeening off part of the filament, the image could be made quite small, so that there was no possibility of the above effect occuring.

(b) For the region 2700 Å.U.—2400 Å.U., the radiation of a tungsten lamp is very feeble, and another arrangement was adopted. An image of the filament (considerably enlarged) was thrown on the slit by means of a quartz lens. This lens was provided with a suitable diaphragm, and an image of the diaphragm aperture was formed on the prism by the lens immediately in front of the slit. Uniform illumination of the slit was secured by the fact that the filament of the lamp was in the form of a flat ribbon, and that the image of this ribbon was considerably larger than the slit.

The widths of the steps were determined by direct measurement with a comparator, and the intensity of the light producing the spectra was directly proportional to the widths so obtained.

An advantage of the method was that, as all six calibration spectra were taken simultaneously, it was not neccessary to run the lamp on constant current; further it resulted in a great saving of time.

Determination of the band intensities in the β system.

Since the highest accuracy was not required in the determination of the intensities of the bands as a whole, it was decided to determine the band head intensities, and to use this as a measure of the total intensity of each band. The band system extends over several hundred Angstrom units, and it was therefore necessary to take the variation in plate sensitivity into account. For this purpose, density marks were made with a lamp in which the energy distribution in the spectrum was known. For the region 2400—3100 Å.U., the quartz band lamp was used, and the intensity distribution was calculated from the colour-temperature. For the region below 2400 Å.U., a smaller quartz spectrograph was used, since the exposures with the large instrument would have been excessively long. It was not found practicable to use the quartz band lamp in this region, as the energy radiated is so small relatively to that in the region of maximum sensitivity of the photographic plate, and much trouble from stray light was experienced. The positive crater of a carbon arc, which with its high temperature has a much more favourable energy distribution, was accordingly used. The researches of Lummer (39) have shown that the temperature of the brightest spot of the crater is independant of current and arc length, and is determined only by the properties of the carbons. Consequently, although not an ideal source, it was possible to take calibration spectra with the arc, using the slit width variation method.

In order to avoid the rapid decrease in sensitivity which occurs in the region 2150 Å.U.—2400 Å.U., oiled plates were used. A mineral oil used for machine lubrication was found suitable, and was applied with the fingers. After some minutes, the coating became fairly uniform. It was found that the sensitivity was everywhere reduced by the oil, but the reduction at 2400 Å.U. was much greater than at 2150 Å.U. The crater colour temperature of the type of carbon employed has been determined in this laboratory, and found to be 4200° K. From this, the energy distribution according to Planck's formula was calculated, the carbon being assumed to be gray.

Since the band heads may be considered as parts of a continuous spectrum (they consist of many superposed lines of different wave-lengths), no correction for dispersion was applied, the dispersion correction being the same for calibration spectra and band heads. The intensities were calculated in the usual way from the calibration curves, with the addition that the variation in intensity of the standard lamp with wave-length had also to be taken into account.

In order to connect the two series of band head intensities, the spectrograph was arranged so that the series overlapped. The intensities in one series were then reduced by the appropriate factor to make them comparable with those of the other series. The reduced results are given in Table V. All the band heads appearing on the plates with exposures up to four hours have been measured; Mulliken lists several, however, particularly in the $v' = 4,5$ and 6 progressions, which did not appear on the writer's plates. At the long-wave end it would probably have been possible to have obtained one or two more members for some of the progressions by photographing the region above 3100 Å.U., but since these bands are not strong, and further the greater plate sensitivity there makes them appear considerably stronger than they really are, is is considered that the effect of these bands on the intensity sum (the determination of which was the object of these measurements) is negligible.

Determination of the Intensity Ratios of the Isotopes.

The ideal method of comparing the intensities of the isotopic bands is to determine the intensity ratio of corresponding lines in the bands. It has been found possible of do this for several bands in the BO spectrum, and the results of this method must be considered to be the most accurate. In some of the weaker bands, however, this is not possible because the structure is not sufficiently developed to give the lines which are well resolved, and only the heads can be seen. These, consisting of about 12 lines of the R branch, are much stronger than the individual lines, as may be seen from the registration (Plate I). It is not, however, permissible to compare the maximum intensities of the heads, as is done in the case of single lines, because the heads of the isotopic bands are not of the same shape, due to the fact that the rotation constants differ.

The only sound way of comparing the intensities of the heads is to determine the shape of the band heads, integrate the intensity over the whole head, and then compare integrated intensities. In order to do this, enlarged drawings of the registrations of the heads were made with the aid of an epidiascope. The densities at a sufficient number of points were then calculated, and the corresponding intensities read off from the density curve. The heads were now re-drawn, the ordinates being the intensities so determined, and the areas under the curves were calculated. The ratio of these areas for isotopic bands gave a value for the intensity ratio which, although not so accurate as a line-for-line comparison, was certainly much more reliable than the ratio of maximum intensities would have been.

Table VI.

Band	0—3	1—4	1—5	2—5	2—6	3—7
Intensity ratio of isotopic band. *a* = from lines *b* = from heads — *a*		3.49	3.41	3.34 3.22 3.49 3.42	3.50 3.17 3.45 3.49	4.30 4.38 4.05
b	3.56	3.20	3.53			
Average	3.56	3.35	3.47	3.37	3.40	4.24
Corrected for plate sensitivity	3.63	3.44	3.56	3.48	3.50	4.37
$\frac{f(E_{v'})}{f(E^i_{v'})}$	1	0.985	0.985	0.95	0.95	1.21
Isotope ratio	3.63	3.50	3.61	3.66	3.68	3.61

Mean ratio = 3.63 ± 0.02.

Corresponding atomic weight = 10.794 ± 0.001 (correcting for O^{17} and O^{18}).

Results of Measurements on the Boron Isotopes.

The intensity ratio of the isotopic bands of BO has been determined by a line-for-line comparison for the 1—4, 1—5 2—5, 2—6 and 3—7 bands, and by comparison of the integrated intensities of the heads for the 0—3, 1—4, 1—5 and 2—5 bands. The latter three were intended as a check on the agreement of the two methods. Some of the bands have been measured on several plates, and the individual values found are given in the second horizontal column of Table VI. The fourth horizontal column of the same table gives the ratios corrected for plate sensitivity.

The most striking feature of the result is the value for the 3—7 band, which is considerably higher than any of the others. No band of BO is known which might be superposed on the main band and so account for a high intensity ratio; on the contrary, however, the observed ratio may be slightly too low, as the 0—5 main band is superposed on the weaker isotope of 3—7. The fact that so many other transitions give a lower ratio must be taken to mean that this also is real, and that considerable differences in the intensity ratio of the isotopes exist.

The most promising method of arriving at an explanation of this fact appears to lie in a determination of the excitation function $f(E_{v'})$ of the molecule. Mulliken has already pointed out (33) that the excitation of BO with active nitrogen is non-thermal, and from eye estimates of the intensities of the bands, he was able to form some idea of the distribution of the molecules among the different initial vibrational states. It seemed, however, highly desirable to make measurements of the band intensities in order to determine the function more accurately, since eye estimates may be quite misleading when a considerable range of wave-lengths is involved, and the measurements of the band head intensities described above were therefore made.

The sum of all the intensities of the bands in each v'' progression (i.e. a progression in which v' constant) may be represented by

$$\Sigma I = f(E_{v'}) \left[p_{v'\text{-}0} + p_{v'\text{-}1} + p_{v'\text{-}2} + \ . \ . \ . \ \right]$$

where $f\ (E_{v'})$ is the number of emitters in the v' state, and $p_{v''\text{-}0}$ etc. are the transition probabilities for the various bands. It is required to find the values of $f\ (E_{v'})$ for the various progressions, the band intensities being known.

In the application of the summation rule in atomic multiplets, the number of emitters (statistical weight) in a given sub-level in the upper state is obtained by summing up the intensities of lines due to transitions from that state. Actually, not the intensities, but the square of the amplitude of the virtual oscillators are summed up, and these are obtained by dividing the intensity of each line by ν^4, ν being the frequency of the line in question.

The transition probabilities p are different for the different v'' progressions, but we may assume that the sum of all the p — values will not be very different for the different progressions. Making this assumption, we obtain the relative values of $f\ (E_{v'})$ by summing up I/ν^4 for each progression.

Whether I/ν^4 or even simply I is used makes actually very little difference to the shape of the resulting curve when these quantities are plotted against $E_{v'}$. This is because each progression is displaced with respect to its neighbours by a frequency interval which is small compared with the band frequencies.

Table V.

Intensities of Band Heads in β system of BO.

Band	Int.	ν^4	I/ν_4	Band	Int.	ν^4	I/ν^4
0—0	90	33	2.7	1—0	127	38	3.3
0—1	78	28	2.8	1—1	26	32	0.8
0—2	77	24	3.2	1—2	—	27	—
0—3	28	20	1.4	1—3	59	22	2.7
0—4	14	16	0.9	1—4	50	18	2.8
0—5	—		—	1—5	29	15	1.9
				1—6	14	12	1.2
Sum			11.0				12.7
2—0	400	42	9.5	3—0	125	47	2.7
2—1	—	36	—	3—1	98	40	2.5
2—2	124	31	4.0	3—2	—	34	—
2—3	42	25	1.7	3—3	20	29	0.7
2—4	17	21	0.8	3—4	77	24	3.2
2—5	103	17	6.1	3—5	—	20	—
2—6	92	14	6.6	3—6	16	16	1.0
2—7	32	12	3.2	3—7	41	13	3.2
				3—8	24	11	2.2
			31.2				15.5
4—5	12	23	0.5				
4—6	10	19	0.5				
4—7	—	16	—				
4—8	7	13	0.5	5—7	7	17	0.4
			1.5				0.4

The sum of the I/ν^4 values for each ν'' progression is given at the foot of the appropriate colums in Table V, and is plotted against the vibrational energy in the upper state in fig. (4).

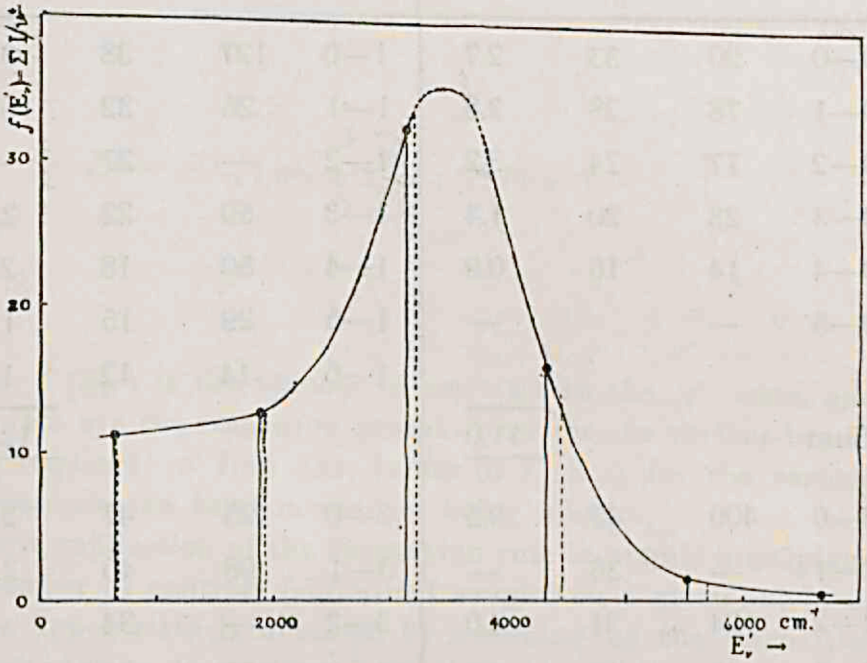

Fig (4) — Excitation Function of BO excited by Active Nitrogen.

The remarkable shape of the curve shows that the excitation is strongly selective, with a very pronounced maximum between $v' = 2$ and $v' = 3$. It is at once apparent that, if the premises of Chap. I are correct, we may expect that $f\ (E'_{v'})$ will differ very considerably for the two isotopes. The vibrational energy levels of the isotope B^{10} are indicated by the dotted lines; on account of the fact that the energy of the lowest level is not zero but possesses a half quantum of energy an isotopic separation exists in this level also. The form of the $f\ (E_{v'})$ curve is such that it cannot be accurately determined from the few points available, and in particular the position of the maximum is very uncertain. Nevertheless, results of considerable value may be deduced from it.

We assume that the values of $f\ (E_{v'})$ for $B^{10}O$ are given by the intersection of the dotted lines with the curve for $B^{11}O$.

It is evident that the number of molecules of $B^{10}O$ which are brought into the $v' = 3$ state is about 17% smaller than the number of $B^{11}O$ molecules in the same state (quite apart, of course, from the real relative abundance of the isotopes), whereas in the $v' = 2$ state, the $B^{10}O$. molecules preponderate by about 4%. In the other vibrational states, the differences are almost inappreciable. The effect of this, of course, is to make the ratio of isotope intensities greater for $v' = 3$, than for the other values of v', just as has been found experimentally, and in this way the variation of intensity ratio of the isotopes is explained.

In Table VI, the values of $\frac{f(E_{v'})}{f(E^i_{v'})}$ and the corrected values of the relative abundance $\frac{A}{A^i}$ are given. The agreement of these latter for the different bands measured is very satisfactory.

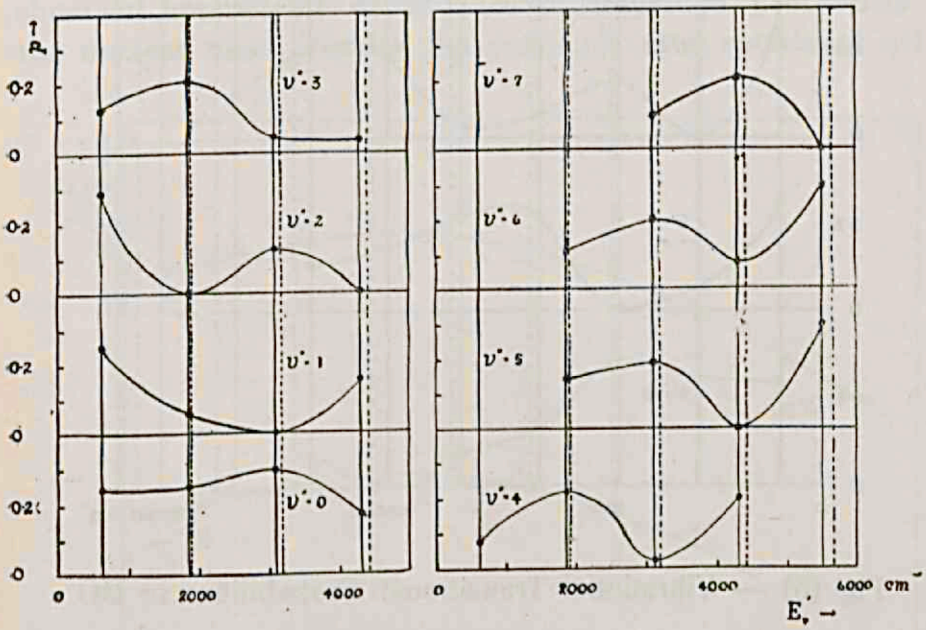

Fig (5) — Vibrational Transition Probabilities in BO.

The possibility of the vibrational transition probabilities p being appreciably different for the two isotopes must now be considered. The relative transition probabilities are obtained by dividing the band intensities by the relative number of molecules in the initial state (i.e. by the intensity sums in Table V). These are plotted as a function of $E_{v'}$ in fig (5), and as a function of $E_{v''}$ in fig. (6). The full and dotted vertical lines represent the vibrational energy levels of the main and isotopic molecules, respectively. Considering first fig. (5), it may be seen that, for the bands measured, there is no appreciable difference in *p* for the isotopes. Consequently the transition probabilities are not influenced by the isotopic separations of the upper level.

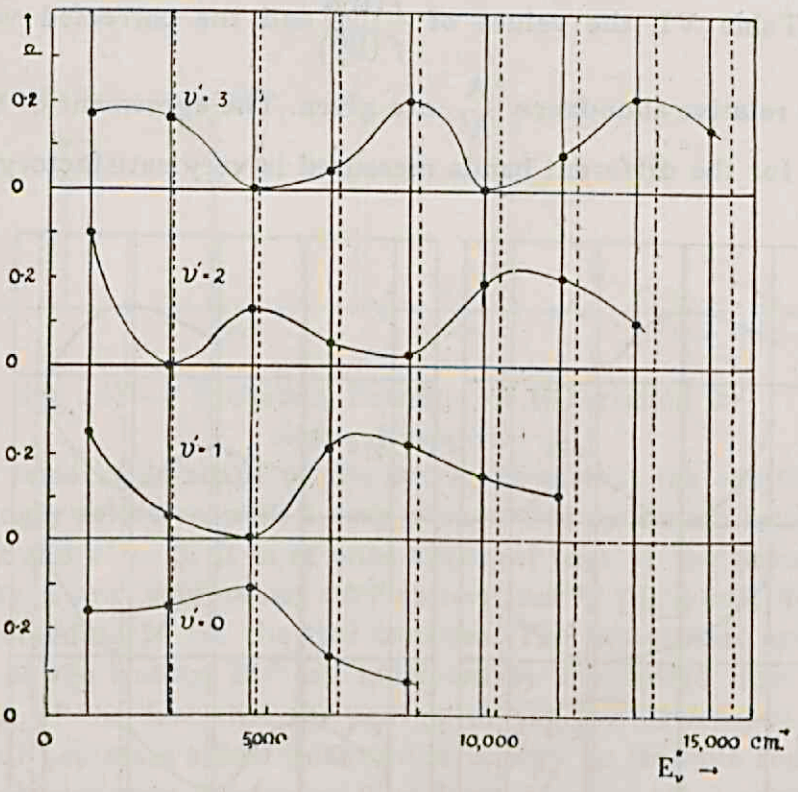

Fig (6) — Vibrational Transitional Probabilities in BO.

Turning now to fig. (6), these curves may be expected to give directly the values of *p* for the isotopes. For the 2—5 and 2—6 bands, therefore, we should expect from this curve that the measured ratio would be approximately 7% lower and 7% higher, respectively, than the true ratio. Actually, however, Table VI shows that these bands give isotopic ratios differing by only ½ %. The isotope ratios for these bands (which are strong and capable of accurate measurement) are considered to be very reliable, and the predicted difference in intensity ratio must therefore be considered to be in error. The fact that all the bands measured give ratios which (when corrected for the differences in the number of molecules of both isotopes in the excited state) are in excellent agreement, may perhaps be taken as evidence against the variation of p for the isotopes. It is not at all certain whether the transition probability may be represented by a smooth curve drawn through the points in figs. (5) and (6).

It may be remarked that in fig. (6), three maximum values of p occur for the states $v' = 3$ and 2 respectively, whereas in general only two (21) are to be expected. Until more is known about the transition probability for vibrational transitions, we may consider that the direct experimental evidence does not show an appreciable dependance of transition probability on the nuclear mass. Finally the existance of a rotational effect

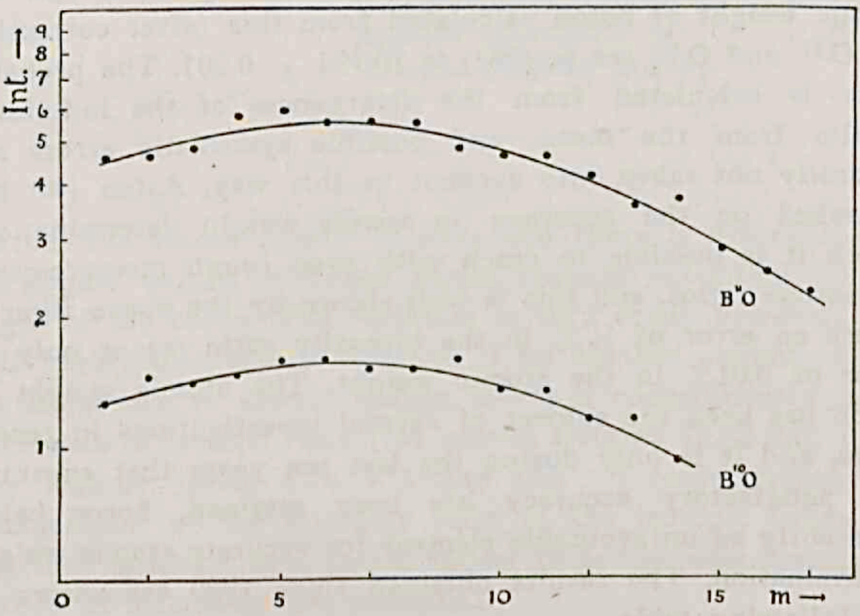

Fig (7) — Line Intensities in 2—6 band of BO
(*m* in arbitrary units).

similar to the variation of $f\ (E_{v'})$ for the isotopes must be considered. In fig. (7), the intensities of main and isotopic lines in the 2—6 band are plotted on a logarithmic scale against an arbitrary series of numbers. (The true values of the rotational quantum numbers are not known for the bands whose intensities have been measured). The fact that the two curves are separated by a constant vertical interval shows that the isotope ratio remains constant, and consequently no dependance of ratio on rotational state exists.

The Atomic Weight of Boron.

The masses of the boron atoms have been determined by Aston (37) with the mass spectrograph, and are given by him to four places of decimals. The present measurements give the relative abundance of the isotopes as 3.63 ± 0.02, and the atomic weight of boron calculated from this (after correcting for O^{17} and O^{18}, see p. (28)) is 10.794 ± 0.001. The probable error is calculated from the divergences of the individual results from the mean, and possible systematic errors are naturally not taken into account in this way. Aston (40) has remarked on the accuracy in atomic weight determinations which it is possible to reach with even rough measurements of isotope ratios, and this is well shown by the above figures, where an error of ½ % in the intensity ratio means only an error of 0.01 % in the atomic weight. The atomic weight of boron has been the subject of several investigations in recent years, and it is only during the last ten years that anything like satisfactory accuracy has been attained, boron being apparently an unfavourable element for accurate atomic weight determination. The results obtained since 1920 are shown in the following table.

Table VII.

Baxter and Scott (41)	BCl_3 : 3Ag : 3AgCl BBr_3 : 3Ag : 3AgBr		10.82
Hönigschmid and Birckenbach (42)	BCl_3 : 3Ag : 3AgCl		10.82
Stock and Kuss (43)	B_2H_6 : $3H_2$		10.806
Briscoe and Robinson (44)	BCl_3 : 3Ag	Asiatic boron	10.818
	BCl_3 (density)		10.817
	B_2O_3 (density)		10.818
	BCl_3 : 3Ag	Californian boron	10.841
	BCl_3 (density)		10.830
	B_2O_3 (density)		10.847
	BCl_3 : 3Ag	Tuscan boron	10.825
	BCl_3 (density)		10.825
	B_2O_3 (density)		10.823
Elliott	Relative abundance of isotopes (Chilian boron)		10.794

From the above, it will be seen that there is evidence that the atomic weight of boron varies slightly according to the origin of the boron. The variation is very small, however, and it is highly desirable to confirm it by another method. Since the difference in atomic weight means a comparatively large difference in isotope ratio (the atomic weights 10.82 and 10.84 give isotope ratios 4.26 : 1 and 4.88 : 1 respectively), the measurement of the intensity ratio of the isotopic bands, as described in this thesis, would appear to be the most promising method of attacking this problem.

Table. VIII.

Vibrational Transition Probabilities in β *system of* BO.

v'' v'	0	1	2	3	4	5	6	7	8
0	0.24	0.25	0.29	0.13	0.08				
1	0.25	0.06	—	0.21	0.22	0.15	0.11		
2	0.30	—	0.13	0.05	0.02	0.19	0.20	0.10	
3	0.17	0.16	—	0.04	0.20	—	0.08	0.21	0.14
4						0.33	0.33	—	0.33

(Corrected for initial distribution of molecules over the different v' states).

Summary.

The factors governing the relative intensities of isotopic bands in molecular spectra are considered, and a theory is given by means of which they may be calculated. It is shown that, in general, the intensity ratio of isotopic bands does not give the abundance ratio of the isotopes directly.

The experimental determination of the intensity ratio of the isotopes Cl^{35-35} : Cl^{35-37} and $B^{11}O$: $B^{10}O$ is described, and a simple method of calibrating photographic plates for intensity measurements is given. The determination of the absolute intensities of the band heads in the β system of BO is also described.

For Cl_2, the experimentally found intensity ratio of the isotopes agrees better with that calculated from the atomic weight when the correction predicted by the theory is applied.

For BO, different intensity ratios of the isotopes are found for different vibrational transitions. When these are corrected for the influence of the peculiar excitation conditions, they agree to a high degree of accuracy. It is thus rendered improbable that the transition probabilities for two isotopic molecules are different, as certain considerations would lead one to suppose. The corrected ratio of intensities of the isotopic bands in BO (3.63 : 1) is lower than that (4.26 : 1) calculated from the accepted atomic weight; the variations in the different determinations of this latter are only slightly smaller than that required to explain this divergence, however.

It is considered that accurate atomic weight determinations may be made in favourable cases by intensity measurements in band spectra.

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Theses.

I.

The granularity of photographic plates plays at least as important a part as the sensitivity in putting a limit to the faintness of spectrum lines measurable by present photometric practice.

II.

Quartz spectrographs for the extreme ultra-violet would be more useful if constructed to use prisms of 10^0 refracting angle instead of the usual 60^0.

III.

It is desirable that the quantity of energy 1 erg/sec./cm.^{2} be adopted as the unit of radiation, and that a name be given to this unit.

IV.

The outline of a theory of the bright lines in stellar spectra given by Milne (Handbuch der Astrophysik, Band III, p. 164-166-170) does not correspond entirely with modern conceptions of the radiation process in stellar spectra.

V.

The apparent absence of series in the spectra of some elements may be due to the variation of intensity ratio of the multiplets.

VI.

The conditions governing the formation of metallic deposits in electrolysis are worthy of closer examination than they have received.

VII.

The result for the nuclear spin of indium round from hyperfine structure observations by Jackson (Proc. Roy. Soc., 128, 508, 1930) is difficult to understand in terms of modern theory.

VIII.

The attempt of Deubner (Phys. Zeits. 20, 909, 1930) to explain the alleged increase in Brownian movement of particles when they are subjected to light (Pospisil, Physikal. Zeits., 31, pp. 65, 78, 447, 1920) cannot be considered successful.