JULY 15, 1930 *PHYSICAL REVIEW* *VOLUME 36*

THE ISOTOPES OF NITROGEN, MASS 15, AND OXYGEN, MASS 18 AND 17, AND THEIR ABUNDANCES

BY S. MEIRING NAUDÉ
RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO

(Received June 9, 1930)

ABSTRACT

I. The isotopes of nitrogen and oxygen.—The absorption spectrum of the NO γ bands, in particular that of the (0, 0) band at $\lambda 2269$, the (1, 0) band at $\lambda 2154$ and of the (2, 0) band at $\lambda 2052$ was studied in search of isotopes of nitrogen and in order to verify the recently discovered isotopes of oxygen of mass 18 and 17.

A hydrogen continuous source was constructed which could be operated by means of a 5 K.W. transformer which gave 0.5–0.75 amps. through the secondary. It was shown that the silvering of the capillary tube joining the electrodes acts as a catalyzing agent which accelerates the recombination of the hydrogen atoms to molecules th increasing the intensity of the continuous spectrum. Owing to a chemical change in the fused quartz window on the hydrogen source which leaves the quartz coloured to a violet tint if light of shorter wave-length than $\lambda 1850$ falls on it, the intensity of the continuous spectrum below $\lambda 2300$ is reduced considerably. This was overcome by using a crystal quartz window which did not show this effect. The photographic plates were sensitized with vaseline.

A glass tube 92 cm long and 5 cm in diameter with quartz windows sealed onto either end was used as an absorption tube. NO was prepared by dropping a solution of $NaNO_2$ into $FeSO_4$ and H_2SO_4.

Band heads were observed in all three bands investigated corresponding to the calculated heads for the four kinds of molecules $N^{14}O^{16}$, $N^{15}O^{16}$, $N^{14}O^{18}$ and $N^{14}O^{17}$, the maximum deviation of the observed wave-lengths from the calculated values being 0.035A. The results obtained therefore provide new evidence for the existence of a nitrogen isotope of mass 15 and verifies the existence of the oxygen isotopes of mass 18 and 17.

II. The relative abundance of O^{16} and O^{18}.—From the atmospheric bands of oxygen Babcock obtained the relative abundance of O^{16} and O^{18} to be 1250 with a probable error of 25 percent. $(O^{16})_2$ is symmetric whereas $O^{16}O^{18}$ is not. This may give different absorption coefficients for the two molecules. This difficulty disappears in NO. By comparing the pressures of NO in the absorption tube at which the (1, 0) P_1 $N^{14}O^{16}$ head could be made to have the same intensity as the P_1 $N^{14}O^{18}$ head the relative abundance of O^{16} and O^{18} was found to be 1075 ± 110.

The relative abundance of N^{14} and N^{15}.—Because in the (1, 0) band the P_1 $N^{15}O^{16}$ head has the same intensity as the head Q_1 $N^{14}O^{18}$ head, the relative abundance of the N^{15} and O^{18} isotopes is inversely proportional to the relative intensity of the P_1 and Q_1 $N^{14}O^{16}$ heads. This relative intensity was found to be 0.65 ± 0.1. The relative abundance of N^{14} and N^{15} is therefore 1075×0.65 or 700 ± 140.

From the relative abundance of O^{16} and O^{18}, and O^{16} and O^{17} the mass of the O^{16} isotope was calculated to be 15.9980 ± 0.0002 if the atomic weight of the mixture of isotopes was taken to be 16.0000. Aston defines the mass of the O^{16} isotope as 16.000 and consequently his atomic weights are higher than the corresponding chemical atomic weights. The chemical atomic weights and Aston's should agree if we correct the O^{16} isotope to an atomic weight of 15.9980 ± 0.0002, that is by 1.25 parts in 10000.

The mass of the N^{14} isotope was calculated to be 14.0069 ± 0.0012 which is in close agreement with Aston's corrected value of 14.0063 ± 0.0029.

THE search for isotopes, especially among the lighter elements is important,[1] because, as is now generally believed,[2] any theory of nuclear structure will have to account for the existence or non-existence of all possible atomic species as well as for the regularities[3] which exist among the different known isotopes. The occurrence of a certain isotope provides evidence that the corresponding configuration of electrons and protons in the nucleus must be stable. The discovery of the oxygen isotopes of mass 18[4] and 17[5] by Giauque and Johnston, and of the carbon isotope of mass 13 by King and Birge[6,7] throws new light on the stability of atoms having the configurations corresponding to these atomic weights.

Recently the author[8] reported that evidence had been found from the absorption spectrum of NO of the existence of the four kinds of molecules $N^{14}O^{16}$, $N^{14}O^{18}$, $N^{14}O^{17}$ and $N^{15}O^{16}$, thus not only verifying the existence of the oxygen isotopes of mass 18 and 17 but also proving the existence of an isotope of nitrogen of mass 15. In the meantime more evidence has been found for the existence of these isotopes. The relative abundance of the isotopic species of an element is considered to be a measure of the relative stability of the different atomic configurations constituting the isotopes. Therefore special care has also been taken to find as accurately as possible the relative abundance of the O^{18} and N^{15} isotopes with respect to O^{16} and N^{14} respectively.

Part I of this paper gives the evidence that has been found for the existence of the isotopes of nitrogen and oxygen, whereas Part II deals with the experiments carried out to find the relative abundance of the isotopes and the conclusions to which the obtained results lead.

PART I. THE ISOTOPES OF NITROGEN AND OXYGEN

Introduction. According to the theory of the isotope effect in band spectra[9,10] a molecule containing a rarer isotope of one of the atoms con-

---

[1] W. F. Giauque, Nature **124,** 265 (1929). At the meeting of the "British Association for the Advancement of Science" held in South Africa in July, 1929, Sir E. Rutherford also pointed out that the determination of all the existing isotopes was one way of studying the structure of the nucleus.

[2] Cf. A. E. Ruark and H. C. Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co,. 1930, p. 39.

[3] W. D. Harkins, J. Am. Chem. Soc. **39,** 856, 870 (1917), Phil. Mag. **42,** 305 (1926), Chem. Reviews, **5,** 371 (1928); Guido Beck, Zeits. f. Physik **47,** 407 (1928), **50,** 548 (1928), **61,** 615 (1930), H. A. Barton, Phys. Rev. **34,** 1228 (1929).

[4] W. F. Giauque and H. L. Johnston, Nature **123,** 318 (1929); J. Am. Chem. Soc. **51,** 1436 (1929).

[5] W. F. Giauque and H. L. Johnston, Nature **123,** 831 (1929); J. Am. Chem. Soc. **51,** 3528 (1929).

[6] A. S. King and R. T. Birge, Nature **124,** 182 (1929); Phys. Rev. **34,** 376 (1929).

[7] R. T. Birge, Phys. Rev. **34,** 379 (1929).

[8] S. M. Naudé, Phys. Rev. **34,** 1498 (1929); **35,** 130 (1930).

[9] R. S. Mulliken, Phys. Rev. **25,** 119 (1925).

[10] In a Symposium of the Faraday Society held September 1929 on Molecular Spectra and Molecular Structure, Birge discusses methods by which the calculation of the rotational effect can be made more accurate. In this work the approximate formula given in Eq. (2) suffices as the analysis of the NO spectrum made use of here contains relatively large probable errors.

stituting the ordinary molecule, gives rise to a displaced band which corresponds exactly to that which originates from the ordinary molecules. The position of the displaced isotopic band can be calculated accurately by taking into account firstly, the displacement due to vibration:[11]

$$\nu_2^v - \nu_1^v = (\rho - 1)\left[\omega_e'(v' + \tfrac{1}{2}) - \omega_e''(v'' + \tfrac{1}{2})\right] - (\rho^2 - 1)\left[\omega_e'x'(v' + \tfrac{1}{2})^2 - \omega_e''x''(v'' + \tfrac{1}{2})^2\right] \tag{1}$$

and secondly, the displacement due to rotation:

$$\nu_2^r - \nu_1^r = (\rho^2 - 1)\nu_1^r \tag{2}$$

where ν_1 refers to the ordinary molecule $N^{14}O^{16}$ and ν_2 to the isotopic molecule, e.g., $N^{15}O^{16}$, $\rho^2 = (\mu_1/\mu_2)$ where $'\mu_1 = 1/M_1 + 1/M_2$ and $'\mu_2 = 1/M_1 + 1/M_2'$, M_1 being the mass of the atom which is common to both molecules, and M_2' being the mass of the rarer of the isotopic species M_2 and M_2', and where ω_e', $\omega_e'x'$, ω_e'', $\omega_e''x''$ are vibrational constants in the initial and final states respectively, and v' and v'' are the vibrational quantum numbers in these states.

The absorption spectrum is far superior to the emission spectrum for studying the isotope effect in a gas containing a rare isotope, for by increasing the length of the absorption tube and the pressure of the gas in the tube, the number of molecules in the path of the light can be increased practically indefinitely, and hence also the number of molecules containing a rare isotope. The lower the pressure, the sharper the absorption lines that are obtained. Therefore the absorption tube is chosen as long as possible and then the pressure of the absorbing gas is raised until the expected effect, if present, is observed.

The absorption spectrum of NO, especially the (0, 0) band at λ2269, the (1, 0) band at λ2154 and the (2, 0) band at λ2052A, that belong to the γ system which is degraded towards the violet, offers a good opportunity for studying the isotope effect. This system of NO has been analyzed partly by Frl. M. Guillery[12] and partly by R. Schmid.[13] Schmid worked on the (0, 0) and (1, 0) bands mentioned. The γ system of NO has a $^2\Pi$ lower level and a $^2\Sigma$ upper level. The separation of the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels has been found to be 124.4 cm^{-1}. Because the $^2\Sigma$ level is single, every band will exist of a doublet, each having a Q and a P head.[14] Of the (1, 0) band Schmid[13] was able to measure only the Q_1 heads. The position of the P_1 heads could, however, be calculated with the help of the relation:

$$Q_1(J+1) - \Delta F'(J) = P_1(J) \tag{3}$$

---

[11] The notation used here is in accordance with the report of Prof. Mulliken to be published in the Phys. Rev. Cf. also R. S. Mulliken, Reviews of Modern Physics **2**, 60 (1930).

[12] Frl. M. Guillery, Zeits. f. Physik **42**, 121 (1927).

[13] R. Schmid, Zeits. f. Physik **49**, 428 (1928).

[14] To avoid confusion the older notation for the heads according to Schmid is used here. The more recent nomenclature of these band heads is given by R. S. Mulliken, Phys. Rev. **32**, 413 (1928).

given by him for the final state. This calculation gives 46391.3 cm^{-1} for the wave-number of the P_1 head which agrees with the measurements made in the course of the present work. The position of the P_1 and Q_1 heads of the (2, 0) band were calculated to be 48708.6 and 48736.1 cm^{-1} respectively. The vibrational constants ω_e, $\omega_e x$, used in computing the vibrational isotopic shift of the band heads, were calculated from the ω_0 and $\omega_0 x$ given by Birge:[15] $\omega_e = \omega_0 + \omega_0 x$ and $\omega_e x = \omega_0 x$. The values thus found were $\omega_e' = 2365$, $\omega_e'' = 1902.19$, $\omega_e' x' = 13$, $\omega_e'' x'' = 13.88$. The calculated shifts with the corresponding wave-lengths are given in columns 4 and 5 of Table I.

The continuous source. As continuous light source a hydrogen lamp was constructed of Pyrex glass according to Bay and Steiner.[16] The source could be operated with a 5 K.W. transformer giving from 0.5 to 0.75 ampere through the secondary. This gave a very intense continuous spectrum. The source was provided with a quartz window at either end. The second window allowed one to sight through the hydrogen source, thus greatly facilitating the lining up of the source, the absorption tube and the spectrograph, which is very important in the case of a long absorption tube, for in this way the maximum intensity can be obtained.

Some experiments were carried out to find out what function was fulfilled by the silvering of the capillary tube which joins the electrodes and in which the discharge takes place, as no conclusions were made in this respect by Gehrcke and Lau[17] who first describe its use. It was found that, when the capillary tube was not silvered the discharge was distinctly red due to the H_α line becoming very prominent. On the other hand, when it was silvered the secondary and also the continuous spectrum of hydrogen which is emitted by the hydrogen molecule,[18] became much stronger, H_α being reduced to about the same intensity as that of the secondary spectrum. The evidence thus points to the mechanism of the silvering being to catalyze the recombination of hydrogen atoms into which the molecules dissociate on giving out the continuous spectrum back to molecules, thus strengthening the secondary spectrum and hence also the continuous spectrum.

As is well known[16] the observed intensity of the hydrogen continuous spectrum falls off rapidly below λ2400A. Experiments were carried out to determine the cause of this phenomenon. It was noticed that a fused quartz window sealed onto the hydrogen tube gave a very strong fluorescence[19] when the tube was in operation. After a window had been in use for about a week, it was replaced by a new one. It was then noticed that the used one had been discoloured to a violet tint, the pattern in it being the same as the one that was seen in fluorescence while the tube was in use. The hydrogen tube was now refilled and sealed off. Two absorption pictures were taken on the

---

[15] R. T. Birge, "Molecular Spectra in Gases" p. 232.

[16] Z. Bay and W. Steiner, Zeits. f. Physik **45**, 337 (1927); see also E. O. Lawrence and N. E. Edlefsen, Rev. Scientific Instruments **1**, 45 (1930).

[17] E. Gehrcke and E. Lau, Ann. d. Physik [IV] **76**, 675 (1925).

[18] J. G. Winans and E. C. Stueckelberg, Proc. Nat. Acad. Sci. **14**, 867 (1928).

[19] H. W. Webb and Miss Helen Messenger, Phys. Rev. **34**, 1463 (1929).

same photographic plate, the first with the used quartz window and the second with an unused window in the light path. It was found that the used window absorbed very strongly in the region below λ2400A. The used quartz window had to be ground down to about half the original thickness before the violet tint was removed. It is not known what the cause of this colouring is, but it seems likely that the SiO_2 constituting the quartz dissociates, giving free silicon. The wave-length causing this fluorescence must be shorter than λ1850, the shortest wave-length transmitted by quartz, because the fused quartz windows used on the absorption tube showed no fluorescence and when the windows were removed after being in use for six months, no violet colouring could be observed. A crystal quartz window was ground and polished and used to replace the fused quartz window on the hydrogen source. The fluorescence in this window was distinctly less conspicuous and the intensity of the continuous spectrum obtained was much better. This window showed no violet colouring even after being in use for three months. It is therefore advisable to use crystal quartz instead of fused quartz windows on the hydrogen source for work in the far ultraviolet.

Procedure. A tube 92 cm long and 5 cm in diameter and with two quartz windows sealed onto either end served as absorption tube. The NO gas was prepared by dropping $NaNO_2$ into a solution of H_2SO_4 and $FeSO_4$. The end of the dropping funnel was well below the surface of the liquid so that all the NO_2 formed could be reduced to NO by the $FeSO_4$. The NO gas was left over the $FeSO_4$ for about a day so that the gas obtained was practically free from NO_2. The NO gas was dried by passing it through a tube containing P_2O_5. The pressure of the gas could be determined by means of a McLeod gauge.

An E1 Hilger spectrograph was used which had a dispersion varying from 1 mm = 1.9A at λ2269 to 1.3A at λ2052. The time of exposure varied from six to twelve hours. The best pictures were taken with 2 cm pressure of NO in the absorption tube. Speedway and Eastman 40 plates were used. The copper arc lines measured by Mitra[20] and corrected by Shenstone[21] were used as comparison spectrum. In the region below λ2100 the copper lines as given by Sommer[22] are less accurately measured and consequently the measurements on the (2, 0) band are less accurate.

The insensitivity of the photographic plate in this region, λ2300 to 2000A, was overcome by using a solution of five grams of vaseline[23] in half a liter of petroleum ether[24] as sensitizer according to Beach.[25] The solution was prepared and kept in a glass bottle. Before taking an exposure the photo-

---

[20] S. K. Mitra, Ann. de Physique **19**, 315 (1923).

[21] A. G. Shenstone, Phys. Rev. **28**, 449 (1926).

[22] L. A. Sommer, Zeits. f. Physik **39**, 711 (1926).

[23] The vaseline used was the ordinary white product of Chesebrough Mfg. Co.

[24] The best results were obtained with petroleum ether made by the Mallinckrodt Chemical Works.

[25] A. C. G. Beach, Nature **123**, 166 (1929); Cf. also H. R. Harrison J. Opt. Soc. Am. **11**, 341 (1925).

graphic plate was dipped into the solution which had been previously poured into a flat dish. On taking it out an oscillatory movement was carried out in order to dry it in such a way that the film of vaseline formed on the surface of the plate after the petroleum ether had evaporated, should be as even as possible. An even film of vaseline was essential especially where a comparison was made between the intensity of two photographs on the same plate (as described in Part II), since the thickness of the film of vaseline determines the intensity obtained.

The plate was then inserted into the holder and the photograph taken in the ordinary way. Before the plate was developed, the vaseline was removed by rubbing its surface with cottonwool which had been soaked in acetone. The plate was then developed as usual.

Results. In all three bands bandheads are observed corresponding to the four types of molecules $N^{14}O^{16}$, $N^{15}O^{16}$, $N^{14}O^{18}$ and $N^{14}O^{17}$ except in the (0, 0) band where, owing to the smallness of shift and the proximity of the $N^{15}O^{16}$ head, the much weaker $N^{14}O^{17}$ head is not observed.

The results are tabulated in Table I being the average of the measurements on five different plates taken at different pressures.

TABLE I.

Band	Nomenclature wave-length and wave-number of $N^{14}O^{16}$ head		Type of molecule containing an isotope	Calculated shift $\nu_2-\nu_1$ in cm^{-1}	Calculated wave-length in A	Observed wave-length in A
0,0	P_1	2269.40	$N^{14}O^{17}$	−2.595	2269.53_4	—
		44050.8_{58}	$N^{15}O^{16}$	−3.375	2269.57_4	2269.56
			$N^{14}O^{18}$	−4.952	2269.65_5	2269.69
1,0	Q_1	2153.63	$N^{14}O^{17}$	−35.193	2155.26_4	2155.23
		46418.5_{77}	$N^{15}O^{16}$	−45.729	2155.75_4	2155.73
			$N^{14}O^{18}$	−67.030	2156.74_5	2156.75
	P_1	2154.90	$N^{14}O^{17}$	−34.444	2156.49_3	2156.49
		46391.3	$N^{15}O^{16}$	−44.758	2156.95_7	2156.98
			$N^{14}O^{18}$	−65.615	2157.94_9	2157.98
2,0	Q_1	2051.01	$N^{14}O^{17}$	−66.401	2054.00_6	2054.02
		48736.1	$N^{15}O^{16}$	−86.282	2054.84_5	2054.82
			$N^{14}O^{18}$	−126.482	2056.54_5	2056.54
	P_1	2052.43	$N^{14}O^{17}$	−65.646	2055.13_5	2055.15
		48708.6	$N^{15}O^{16}$	−85.304	2055.96_5	2055.97
			$N^{14}O^{18}$	−125.055	2057.64_9	2057.66

In the preliminary publication[8] mention was made of faint absorption bands appearing beyond the isotopic heads in the (1, 0) band, whose positions seemed to agree with the values calculated for a possible $N^{16}O^{16}$ head. This point has been the subject of further research. When the focus of the spectrograph was shifted so as to include the (2, 0) band, it was found that the β bands of NO[26] which originate from the same $^2\Pi$ ground state as the γ bands, but have an upper $^2\Pi$ level different from the $^2\Sigma$ upper level of the

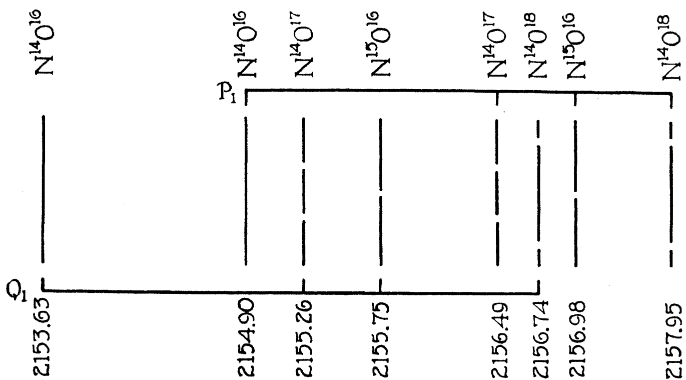
---

[26] F. A. Jenkins, H. A. Barton and R. S. Mulliken, Phys. Rev. **30**, 150 (1927).

γ bands, also appear in absorption although very weakly. Now it happens that the heads of the R and P branches of the (1, 0) β band fall at λ2153.45 and 2153.68A and thus on top of the (1, 0) γ band. Consequently these heads do not interfere with the isotopic bandheads. Because the β system is degraded towards the red, its rotational fine structure appears beyond the isotopic heads. The position of these rotational lines can be calculated from the relation

$$F = \text{const} + Aj + Bj^2 + Cj^3 + Dj^4$$

given by Jenkins, Barton and Mulliken.[26] All the observed absorption lines beyond the heads of the isotopic molecules could be accounted for in this way. The isotope N^{16} does therefore not exist (unless it is less abundant than O^{17}) especially since the (2, 0) band shows definitely no trace of the N^{16} isotope. The evidence the (1, 0) band gives for the other isotopes is, however, not effected by these faint absorption lines since the intensity of the isotopic heads is much greater than the rotational fine structure of the (1, 0) β band.



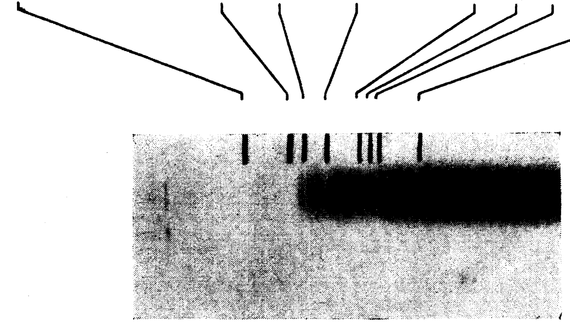


Fig. 1. The expected appearance of the band-heads of the (1, 0) band are sketched. The types of molecules giving these band-heads are given on the upper side of the figure and on the lower side the corresponding wave-lengths of the heads are given. The line on the lower side of the figure joins the Q_1 heads formed by the different types of molecules, whereas the upper line joins the corresponding P_1 heads.

Fig. 2. An enlargement of the observed appearance of the (1, 0) band. The positions of the band heads are indicated by lines which connect the heads to the corresponding heads in Fig. 1.

Because the P_1 and Q_1 heads of the (1, 0) band are separated by 27.3 cm^{-1} and the smallest displacement, namely that of the Q_1 head due to the $N^{14}O^{17}$ molecule is -35.193 cm^{-1}, one expects the six heads due to $N^{14}O^{17}$ $N^{15}O^{16}$ and $N^{14}O^{18}$ all to fall beyond the $N^{14}O^{16}$ P_1 head and to be observable as far as they do not overlap one another. In Fig. 1 a sketch is given of the expected appearance of the bandheads. In Fig. 2 a photograph (enlarged eight times) of the actual appearance of the (1, 0) band is reproduced. This photograph was taken with a pressure of 2 cm of NO in the 92 cm absorption tube, the time of exposure being ten hours.

Between the Q_1 $N^{14}O^{17}$ and $N^{15}O^{16}$ heads a faint absorption line is seen which could be shown to be due to the overlapping of three lines of the rotational structure belonging to the Q_1 $N^{15}O^{16}$, and $N^{14}O^{18}$ heads and the P_1 $N^{15}O^{16}$ head. The P_1 $N^{14}O^{17}$ head is not visible in this picture but in pictures taken at higher pressures one is able to observe and measure it accurately.

The separation of the P_1 and Q_1 heads in the (2, 0) band is 27.5 cm^{-1} The displacement of the Q_1 $N^{14}O^{17}$ head is calculated to be 66.401 cm^{-1} and will therefore fall beyond the P_1 $N^{14}O^{16}$ head. All the isotopic heads are therefore expected to fall beyond the P_1 head. As can be seen from the calculated positions of these heads in column 5 of Table I, they are widely separated and can therefore be measured more accurately. The increased insensitivity of the photographic plate, however, makes a reproduction of the obtained pictures impossible.

The fine structure of the isotopic bands could also be measured when the overlapping was not too much. This corresponded very closely with the rotational fine structure of the main heads, so that it provides further decisive evidence that these heads must be due to the isotopic molecules.

To be absolutely sure that these bands might not perhaps be due to some other molecule, e.g. $(NO)_2$, the absorption tube was replaced by a tube 1.2 cm in length and filled up to 75 cm pressure with NO. The light passing through this tube has to traverse about the same number of molecules of NO as in the case of the 92 cm tube with 1 cm pressure. If $(NO)_2$ molecules were present their concentration should increase with the square of the pressure and the path being 75 times shorter, one would expect the effect due to these molecules to be 75 times as intense. The absorption of the isotope heads observed is quite similar to that obtained with the 92 cm tube, except that they are a little more diffuse, as one might expect owing to the high pressure. The measured shift agrees accurately with the above results.

This investigation therefore definitely proves the existence of an isotope of nitrogen of mass 15 and verifies the existence of the recently discovered isotopes of oxygen of mass 17 and 18.

PART II. THE ABUNDANCE OF O^{18} AND N^{15}

The relative abundance of O^{16} and O^{18}. The abundance of the oxygen isotope of mass 18 has been determined by Babcock[27] from the atmospheric

---

[27] H. D. Babcock, Proc. Nat. Acad. Sci. **15**, 471 (1929); Phys. Rev. **34**, 540 (1929).

bands of oxygen. Babcock took an absorption picture of the atmospheric bands using the sun as continuous light source and the oxygen in the atmosphere as his absorbing medium. In this way the heads of the displaced bands due to the $O^{16}O^{18}$ molecule could be photographed. On the same plate he took an absorption picture of the corresponding main bands due to $(O^{16})_2$ using a certain length of air path in the laboratory for the absorption. When the isotopic heads in the former appeared to him to be of the same intensity as the main heads in the latter picture, he concluded that the abundance of the molecules giving these bands should be inversely proportional to the number of oxygen molecules traversed in each case. The latter could be calculated from the known path lengths. In this way a relative abundance of one O^{18} isotope in every 1250 O^{16} was obtained as the weighted mean of 1175 and 1350.

The molecule $(O^{16})_2$ is symmetric whereas $O^{16}O^{18}$ is unsymmetric. These molecules may have different absorption coefficients which would affect the results obtained for the relative abundance. This difficulty disappears in the case of NO, for both $N^{14}O^{16}$ and $N^{14}O^{18}$ are unsymmetric. A redetermination of the abundance of O^{18} therefore seemed desirable.

The pressure of NO in the absorption tube could be varied thus giving different numbers of molecules in the light path, and could be measured accurately by means of a McLeod gauge. The pictures were taken on the same photographic plate, 5 mm apart, so that the condition of sensitizing and developing were exactly the same. The two pictures could be taken under the same experimental conditions and special care was taken to get the continuous background of the pictures of the same intensity.

The (1, 0) band is the best to apply this procedure to, because the intensity of the plate is still favourable and the displacement of the isotope heads is fairly large. The only displaced head to which the method can, however, be applied with certainty is the $N^{14}O^{18}$ head at $\lambda 2157.98$ corresponding to the P_1 head of $N^{14}O^{16}$ $\lambda 2154.90$. This head is displaced the farthest and consequently there is no overlapping of the fine structure of the less displaced isotopic heads. The fine structure of the (1, 0) β band mentioned above is so weak that it does not affect the accuracy with which the intensity of the displaced isotope head can be estimated.

The first pictures taken showed that the higher pressure caused the isotopic head to appear much broader than expected. Pressure broadening according to Lorentz[28] was at once suspected to be the cause. Two pictures were taken on the same plate, one with only 2.1 cm pressure of NO in the absorption tube, the other with the 2.1 cm of NO left unchanged but with 44 cm pressure of N_2 added, see Fig. 3. Since the N_2 has no absorption bands in this region it can only have the effect of pressure broadening according to Lorentz. A large number of investigators[29] have done work on the pressure

---

[28] H. A. Lorentz, Proc. Amsterdam **8,** 501 (1906). For a discussion of this phenomenon according to the wave mechanics cf. J. Frenkel, Zeits. f. Physik **59,** 198 (1930).

[29] Cf. W. Schütz, Zeits. f. Physik **45,** 30 (1927) and the literature given there.

broadening in the case of atoms, and Teves[30] has extended this work to bands. The pressure in the absorption tube was therefore regulated as follows: If a pressure ratio of 1 to 1000, for instance, was desired, the tube was filled to 5 cm with NO and 65 cm of N_2 added. After an exposure with this pressure was finished, the pressure in the tube was changed to 0.005 cm of NO and 70 cm of N_2, and another picture taken on the same photographic plate. In both cases therefore the total pressure was the same, viz. 70 cms, and a large excess of N_2 was present. N_2 was chosen, chiefly because it has no absorption bands above λ1520A and also because it has about the same molecular radius as NO[31], the latter factor influencing the broadening according to Lorentz and Frenkel. It was absolutely necessary to have N_2 free from all traces of oxygen otherwise NO_2 would be formed in the absorption tube and this molecule gives a continuous absorption in the region in question. Pure N_2 was obtained by heating sodium azide in a flask from which all the air had been exhausted beforehand. The gas was then dried in a tube containing P_2O_5. Pictures were taken with pressure ratios varying between 1 in 1800 and 1 in 500. Definite differences in the intensity of the absorption of the main and isotopic heads were found for all ratios outside 1 in 990 and 1 in 1160. Within this region ten photographs were taken at different pressure ratios, but, as it is difficult to decide definitely about their intensities, an average is taken over all ten values giving as result a relative abundance

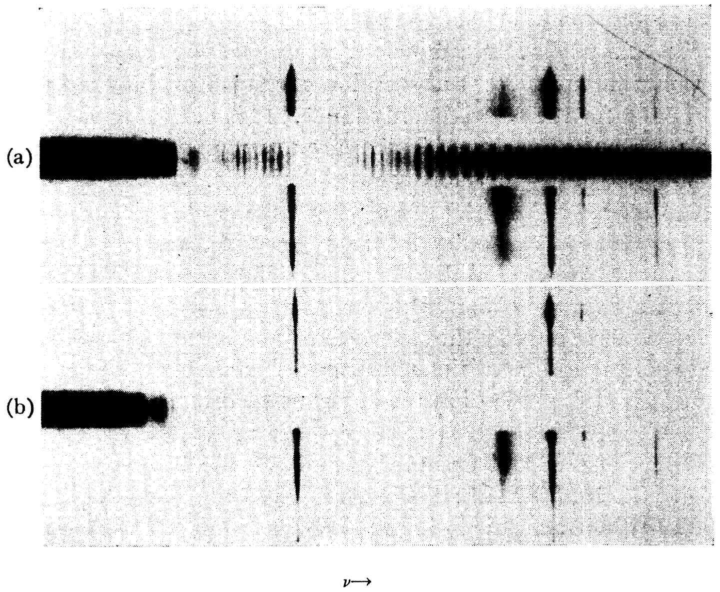


Fig. 3. (a) Absorption picture with 2.1 cm NO pressure. (b) Absorption picture with 2.1 cm NO+44 cm N_2 pressure. A comparison shows that in (b) every rotational line is broadened so much that the absorption becomes complete.

[30] M. C. Teves, Zeits. f. Physik **48,** 244 (1928).

[31] P. M. Morse, Phys. Rev. **34,** 57 (1929).

of O^{18} of one in every 1076 O^{16} atoms. Taking the mean of the two extreme ratios where definite differences of the same amount could be observed in the intensities a ratio 1/1075 is found for the abundance. Although the first calculation gives a probable error of only three percent, the maximum error is given as ten percent, as systematic errors might occur in the method used. The abundance ratio of O^{16} to O^{18} is therefore given as 1075 ± 110.

After obtaining the above result two comparison pictures were taken with helium instead of N_2 to make sure that no resonance effect between NO and N_2 was present. The pictures indicated that the given abundance ratio was correct.

The result differs by about 14 percent from that given by Babcock, but as Birge[32] gives a probable error of 25 percent for Babcock's values this deviation does not seem too large. Further, Babcock compares the absorption of the oxygen in the laboratory and hence at atmospheric pressure with the oxygen in the atmosphere where the pressure varies exponentially to zero. Hence the pressure broadening which, as pointed out above, is very great, is much more effective in the first case where all the oxygen is at atmospheric pressure than in the second case where only the oxygen near the ground is at atmospheric pressure. This would give a result which would differ from the one obtained with the same pressure in both cases in the sense of the result found here.

Babcock finds the relative abundance of O^{18} and O^{17} to be eight to one. If a maximum error of ten percent is allowed for this value and the relative abundance of O^{16} and O^{18} is assumed to be 1075 ± 110 as found here, the relative abundance of O^{16} and O^{17} becomes 8600 ± 1750.

The relative abundance of N^{14} and N^{15}. As stated above the overlapping of the fine structure due to the $N^{14}O^{18}$ molecule, made it impossible to determine the abundance of the $N^{15}O^{16}$ molecule in the same way. Here the circumstance that the $Q_1N^{14}O^{18}$ and $P_1N^{15}O^{16}$ heads lying close together are of the same intensity was made use of. At very low pressures practically no fine structure of the isotopic heads is present and therefore the conclusions following this observation are rigid. It was further noticed that the $P_1N^{15}O^{16}$ head was more intense than the $Q_1N^{15}O^{16}$ head. This resulted from the fact that the main $P_1N^{14}O^{16}$ head was less strongly absorbed than the corresponding Q_1 head. The ratio of the main P_1 and Q_1 heads could easily be determined by taking different pressures in the absorption tube and observing at which pressures the heads had the same intensity. The ratio of these pressures was found to be 0.65 ± 0.1 and this is evidently the intensity ratio of the main heads, the P_1 head being less intense. This result could also be verified by taking microphotometer curves of the heads with a Moll apparatus and averaging the area under each of the heads. This result agreed accurately with the above result. The fact that the $Q_1N^{14}O^{18}$ and $P_1N^{15}O^{16}$ heads are equally intense can therefore only be ascribed to the fact that the $N^{14}O^{18}$ must be less

---

[32] R. T. Birge, Phys. Rev. Suppl. 1, 69 (1929).

abundant than the $N^{15}O^{16}$ in the same ratio as the Q_1 head is stronger than the P_1 head.

This result therefore gives us as relative abundance of $N^{14}O^{18}$ and $N^{15}O^{16}$ molecules the ratio 0.65 ± 0.1 and hence as the relative abundance of N^{14} and N^{15} the ratio 1075×0.65 or 700 ± 140. In this case the maximum error is given as 20 percent, since the ratio 0.65 may be affected as much as ten percent by systematic errors.

Discussion. The existence of the O^{18} and O^{17} isotopes seems to be quite certain. This, however, affects Aston's[33] atomic weights determined by means of the mass spectrograph with respect to the chemical atomic weights.[34] Aston assumes the atomic weight of the O^{16} isotope to be 16.0000, whereas the chemical method defines the average atomic weight of the O^{16}, O^{17} and O^{18} isotopes as 16.0000. The actual atomic weight of the O^{16} isotope can now be calculated by making use of the relative abundance determined above. The atomic weight of the O^{16} isotope can be computed from the following relation:

$$1074 \times 8x + 8 \times 18 + 17 = (1075 \times 8 + 1)16.0000 \tag{4}$$

from which we get $x = 15.9980 \pm 0.0002$. We see therefore, that although the maximum error in the relative abundance of the oxygen isotopes is very large, the value of the atomic weight of the O^{16} is little affected. It is easily seen that it makes no difference in the result whether 18 or 17.991,[35] as recently found by Mecke and Wurm to be the atomic weight of O^{18}, is used. If the chemical atomic weight 16.0000 is our standard, Aston should use 15.9980 ± 0.0002 as the atomic weight of the O^{16} isotope, if he expects to obtain an agreement between his values and those obtained by chemical methods. This change in value of the O^{16} isotope used as standard by Aston corresponds to a change of 1.25 ± 0.13 in 10000. This does not mean that Aston's determinations of the atomic weights are less accurate than 1 in 10000 as given by himself, but just gives the amount by which all his values have to be corrected in order to allow a comparison with the values obtained by chemical methods.

We can now proceed to correct Aston's values by 1.25 ± 0.13 in 10000. In Table II the corrected values of Aston are compared with the chemical determinations. The elements chosen are those which have no isotopes as far as we know, or which have rare isotopes, as these are the only cases where a direct comparison is possible.

A comparison of columns 1 and 3 reveals a number of interesting points. In the case of hydrogen a correction of Aston's value makes the agreement wores, but the corrected value can be made to agree with the chemical value by assuming an error of 0.00011 which is well within the maximum error allowed for.

---

[33] F. W. Aston, Proc. Roy. Soc. **115A**, 487 (1927).

[34] Cf. R. T. Birge, Phys. Rev. Supplement **1**, 19 (1929).

[35] R. Mecke and K. Wurm, Zeits. f. Physik **61**, 37 (1930).

TABLE II. *Atomic weights.*[36]

Atom	Chemical method	Aston's mass spectrograph	Aston's values corrected by 1.25 in 10000
H	1.00777 ±0.00002	1.00778 ±0.00015	1.00766 ±0.00016
He	4.0018 ± .0003	4.00216 ± .0004	4.00166 ± .00045
C	12.0025 ± .00019	12.0036 ± .0012	12.0021 ± .0014
N	14.0083 ± .0008	14.008 ± .0028	14.0063 ± .0030
O	16.0000 ± .0000	16.0000 ± .0000	15.9980 ± .0002
F	19.00	19.0000 ± .0019	18.9976 ± .0021
P	31.027	30.9825 ± .0046	30.9786 ± .0050
As	74.96	74.934 ± .010	74.925 ± .011
I	126.93	126.932 ± .025	126.916 ± .027

In the case of He the corrected value agrees to 1 in 30000 with the chemical value 4.0018. This correction therefore does away with a very bad discrepancy between Aston's values and the chemical values. Further, as pointed out by Birge[37] this value agrees accurately with Eddington's[38] calculated value for an ideal rigid nucleus. This agreement might be due to chance as the value still has a large maximum error and hence it cannot be assumed from this that the helium atom really has a rigid nucleus.

Birge and King have recently discovered an isotope of carbon of mass 13. One would therefore expect the chemical atomic weight to be higher than that found by Aston. The reverse is the case, however. If Aston's value is corrected one obtains a value of 12.0021 which is in close agreement with the chemical value 12.0025 and still allows for the presence of the isotope C^{13}. From these values the calculated abundance of the C^{13} isotope is 1 in 2500 but this seems to contradict Birge's[7] results according to which the C^{13} isotopt should be more abundant relative to C^{12} than the N^{15} relative to N^{14}, but the given atomic weights still have a large probable error which may accoun for this discrepancy.

In the case of nitrogen the abundance of the N^{15} has been determined as 1 in 700 ± 140 N^{14} isotopes. From this we can determine what the expected atomic weight of the N^{14} isotope should be, for

$$700x + 15 = 701 \times 14.0083 \pm 0.0008 \tag{5}$$

or

$$x = 14.0069 \pm 0.0012.$$

This value agrees with Aston's corrected determination 14.0063 to within 1 in 20000.

For F, P and As the chemical values are given with less accuracy, but a comparison of Aston's corrected value of P with the chemical value leads

---

[36] Most of the values with their probable errors given in the first column are taken from the excellent discussion by R. T. Birge, Phys. Rev. Supplement **1**, 18 (1929). The values in column 2 with their maximum errors are obtained from Aston's paper, Proc. Roy. Soc. **115A**, 487 (1927). The chemical values for F, P, As and I are taken from the Second Report of the International Committee on Chemical Elements, J. Am. Chem. Soc. **47**, 597 (1925) and the German Committee, Berichte **62**, 1 (1929).

[37] R. T. Birge, Phys. Rev. **35**, 1015 (1930).

[38] A. S. Eddington, Proc. Roy. Soc. **A126**, 696 (1930).

one to suspect the presence of heavier isotopes of P in small quantities. Although less certain, the same seems to be indicated by the corresponding values for F and As.

Until 1928 the German Committee[39] gave the atomic weight of I as 126.92 and Birge[40] finds as weighted average of Clark's values 126.926. This indicates that the real chemical value for I may still be on the lower side of 126.932—the value that is now accepted—and such a value will be in better agreement with Aston's corrected value 126.916.

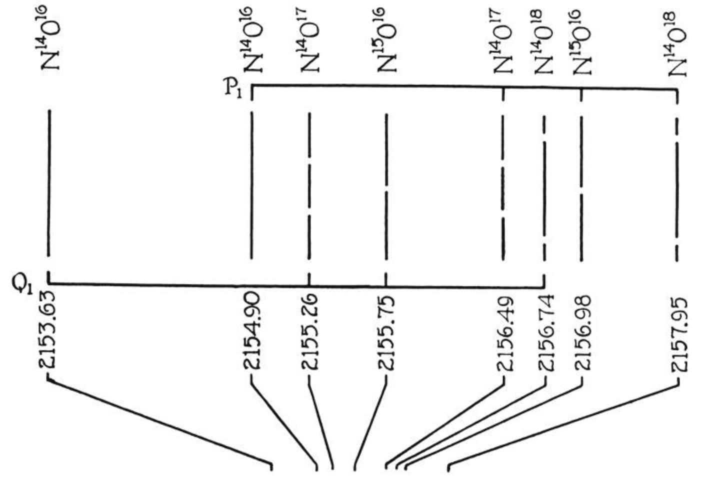
Although it is difficult to draw definite conclusions from the above, it is quite clear that the sooner an agreement is reached by chemists and physicists as to the value which should be used as standard of atomic weight, the less confusion will exist as to the most accurate atomic weights.

Mr. F. Bueso-Sanlehi started this work but had to leave before obtaining any definite results. I wish to thank Professor R. S. Mulliken who suggested the search for isotopes in these NO bands and also wish to thank him and Dr. A Christy for their helpful suggestions and Professor H. B. Lemon for allowing me the use of the apparatus in his laboratory.

---

[39] Max Bodenstein, etc., Berichte **61B**, 1–31 (1928).

[40] R. T. Birge, Phys. Rev. Supplement **1**, 25 (1929).



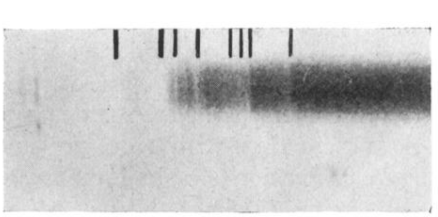


Fig. 1. The expected appearance of the band-heads of the (1, 0) band are sketched. The types of molecules giving these band-heads are given on the upper side of the figure and on the lower side the corresponding wave-lengths of the heads are given. The line on the lower side of the figure joins the Q_1 heads formed by the different types of molecules, whereas the upper line joins the corresponding P_1 heads.

Fig. 2. An enlargement of the observed appearance of the (1, 0) band. The positions of the band heads are indicated by lines which connect the heads to the corresponding heads in Fig. 1.

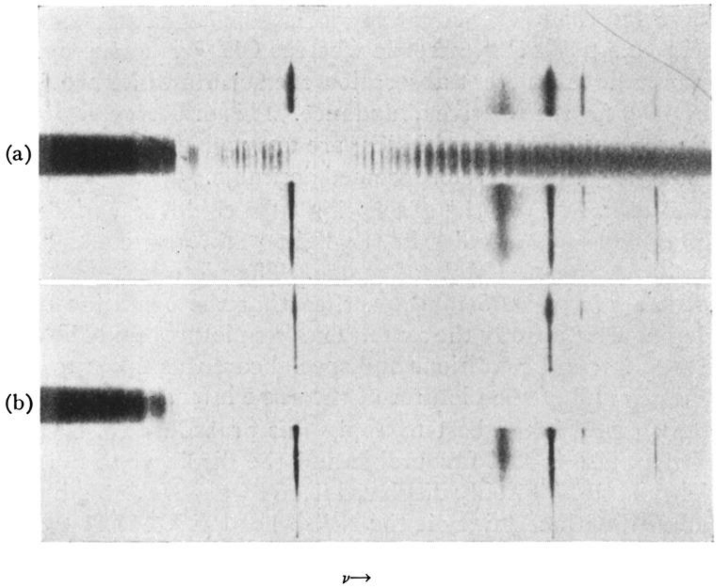


Fig. 3. (a) Absorption picture with 2.1 cm NO pressure. (b) Absorption picture with 2.1 cm NO+44 cm N_2 pressure. A comparison shows that in (b) every rotational line is broadened so much that the absorption becomes complete.