

beobachteten $\Delta l = g(T)$ können wir schliesslich auch das Dipolmoment p als Funktion der Temperatur finden. In bester Übereinstimmung mit der früheren Abschätzung auf $> 10^{-14}$ e.s. Einheiten ergibt sich hier für den grössten Wert an der unteren Grenze des kr. fl. Existenzgebietes etwa $100 \cdot 10^{-14}$ bei einer Orientierung von 80 %, und 1° unterhalb des Klärpunktes noch etwa $10 \cdot 10^{-14}$ bei einer Orientierung von 5 %. Der Wert am Klärpunkt selbst lässt sich wegen der Temperaturverschmierung nicht angeben. Aus diesen Zahlen berechnen sich die Schwarmgrössen $100 \cdot 10^4$ bzw. $5 \cdot 10^4$ Moleküle, und zwar gelten diese Werte auch für Benzophenon, nur eben mit dem Unterschied, dass sie hier innerhalb etwa 2° durchlaufen werden; denn man kann die entsprechende $\Delta\sigma$ -Kurve für Benzophenon mit der Kurve für Azoxyanisol durch eine blossse Veränderung des Temperaturmassstabes völlig zur Deckung bringen.

Kontrollversuche mit Verbindungen ohne Dipolmoment sind im Gange. Die scheinen anzudeuten, dass ebenso wie für die Existenz einer kr. fl. Phase auch für diese vorübergehende Schwarmbildung am Schmelzpunkt das Dipolmoment nicht allein massgebend ist. Jedenfalls zeigt das dipolfreie aber sehr unsymmetrische Naphtalinmolekül ($C_{10}H_{10}$) innerhalb etwa $1^\circ C$ denselben Effekt.

Physics. — *On the Relative Abundance of the Carbon Isotope, C^{13} .* By F. A. JENKINS (Fellow of the JOHN SIMON GUGGENHEIM Memorial Foundation) and L. S. ORNSTEIN. (Communication from the Physical Institute of the University of Utrecht.)

(Communicated at the meeting of December 17, 1932).

Introduction.

The determination of the relative abundance of isotopes by quantitative measurements of band spectrum intensities has now been made for a number of elements. ELLIOTT¹⁾ found the proportions of the chlorine and of the boron isotopes from the absorption spectrum of Cl_2 and from the emission spectrum of BO , respectively. VAN WIJK and VAN KOEVERINGE²⁾ evaluated the abundance ratio of the lithium isotopes by measurements of the Li_2 absorption bands. In the cases of boron and lithium small, but definite, disagreements were found with the values computed from the chemical atomic weights. These are as yet unexplained. Among the elements having isotopes of very low abundance, the $O^{18} : O^{16}$ ratio has been determined by MECKE and CHILDS³⁾, and the $N^{15} : N^{14}$

1) A. ELLIOTT, Dissertation, Utrecht 1930.

2) W. R. VAN WIJK and A. J. VAN KOEVERINGE, Proc. Roy. Soc. **132A**, 98 (1931).

3) R. MECKE and W. H. J. CHILDS, Zeits. f. Physik **68**, 376, 1931.

ratio by MURPHY and UREY¹⁾). These determinations were made from the absorption spectra of O_2 and NO , respectively. The corrections to be applied to band intensities in obtaining the true abundance have been studied with regard to the excitation conditions by ELLIOT²⁾, and with regard to transition probabilities by DUNHAM³⁾. These corrections amount at most to only a few percent. On the other hand, qualitative observations on the isotope bands of nitrogen, by HERZBERG⁴⁾, and of carbon, by KING and BIRGE⁵⁾, have indicated variations of a much greater magnitude, the relative intensity apparently changing by several hundred percent under differing conditions of excitation. Since no theoretical interpretation of such variations has yet been found, we have undertaken to study the question by means of quantitative intensity measurements.

The most definite evidence of these variations is given by KING and BIRGE in the case of the carbon isotope, C^{13} . The presence of this isotope was proved by the discovery⁶⁾ of bands due to $C^{12}C^{13}$, $C^{13}C^{13}$, $C^{13}N^{14}$ and $C^{13}O^{16}$. In the SWAN band system, due to C_2 , the band at λ 4744.5 represents the 1.0 band of $C^{12}C^{13}$, and is favorably placed for a comparison of its intensity with that of the 1.0 band of the main system, $C^{12}C^{12}$, at λ 4737. These bands are produced in many different sources, and the λ 4744 band has been identified in most of these. Thus KING and BIRGE found that it appears in the spectra of the high-temperature electric furnace, of the flame of the MECKER burner, and of the vacuum tube with carbon electrodes containing argon and a trace of hydrogen. It has been also observed by SANFORD⁷⁾ in the spectra of N -type stars, and by BOBROVNIKOFF⁸⁾ in certain cometary spectra. As regards the relative intensity of the isotope band, it appears to be strongest in the stellar spectra, where MENZEL⁹⁾ estimates that the λ 4744 band has 0.2 of the intensity of that at λ 4737. KING and BIRGE give an approximate value of 0.005 in the furnace spectrum, and estimate a somewhat greater figure for the MECKER flame and vacuum tube. In the case of the carbon arc in air, they were unable to find any trace of the isotope band.

Since variations of this magnitude in the abundance of C^{13} in different samples of carbon could at once be dismissed as inconceivable, the phenomenon was attributed to the difference in excitation conditions and, in cases where absorption is involved, to the finite optical thickness of the absorbing layer. Obviously, even if the absorption coefficients of the isotopic molecules are equal, the intensities do not correspond to the relative

1) G. M. MURPHY and H. C. UREY, *Phys. Rev.* **41**, 141, 1932.

2) ELLIOTT, *loc. cit.*

3) J. L. DUNHAM, *Phys. Rev.* **36**, 1553, 1930.

4) G. HERZBERG, *Zeits. f. physik. Chem.* **139**, 43, 1930.

5) A. S. KING and R. I. BIRGE, *Astrophys. Jour.* **12**, 20, 1930.

6) R. I. BIRGE, *Phys. Rev.* **34**, 379, 1929; KING and BIRGE, *loc. cit.*, p. 16.

7) SANFORD, *Publ. Astronom. Soc. Pacific.* **41**, 271, 1929.

8) N. I. BOBROVNIKOFF, *ibid.*, p. 117, 1930.

9) D. MENZEL, *ibid.*, **42**, 34, 1930.

abundance when the layer is of finite thickness. KING and BIRGE suggested that the difference in the excitation of $C^{12}C^{13}$ must be closely connected with the temperature differences, since it appeared that the intensity of the isotope head decreased in the order of increasing temperature. However, if this is the case, the effect must be one which is not at present theoretically explained. If one assumes thermal equilibrium, the BOLTZMANN factor would in this case cause a variation of only 14 percent between room temperature and 6000° K, the temperature of the arc.

Experimental.

§ 1. Our first object was to investigate the spectrum of the carbon arc under various conditions, in order to find if the λ 4744 isotope band could be observed in this source. Following the idea of KING and BIRGE, conditions were chosen under which the arc gives a low effective temperature. Spectra were photographed with prism spectrographs of low and medium dispersion from the arc at low pressure (a few mm. to several cm.) in air and in nitrogen. The effective temperature has been shown ¹⁾ to be low in this case. On some plates indications were found of the presence of λ 4744, but these were not conclusive. Spectrograms were then taken of the light from the alternating current arc near the zero phase, where the current and effective temperature are also low ²⁾. Here again, definite evidence for the presence of the isotope band could not be obtained. The difficulty of observing the isotope band in these cases, if it were present, is due primarily to the faintness of the SWAN bands under these conditions, and to the presence of a strong background of continuous spectrum and overlapping band lines. With the low pressure arc, the CO ÅNGSTRÖM bands in particular interfered with the observations.

An arc in purified argon at 16 mm. between carbon electrodes was next tried. It was found that, upon the introduction of a small amount of hydrogen through a palladium valve, the argon spectrum is suppressed, and an intense emission of the C_2 bands obtained. The CN bands, which are very much stronger than the C_2 bands in the arc in air or nitrogen, are here practically absent, while the CH bands are fairly strong. The C_2 isotope band λ 4744 is easily observed on all the plates from this source. We do not regard this as a specific effect of the presence of argon, but rather as due to the much greater intensity of the C_2 bands relative to the background. In argon, it is true, the distribution of intensity in the rotational structure of the bands corresponds to a very low effective temperature. Besides increasing the intensity of the head relative to the rest of the band, this causes a shortening of the 0.0 band sequence beginning at λ 5165, so that

¹⁾ L. S. ORNSTEIN, H. BRINKMAN and A. BEUNES, *Zeits. f. Physik.* **11**, 12, 1932.

²⁾ L. S. ORNSTEIN, H. BRINKMAN and D. VERMEULEN, *Proc. Amsterdam* **34**, 1, 1931.

it no longer overlaps the λ 4744 band. The latter is therefore more easily observed on this account.

It has been shown by JOHNSON¹⁾ that the carbon arc in pure hydrogen gives the SWAN bands with great intensity, with a rather high-temperature distribution among the rotational states. Our spectrograms of the arc in hydrogen at atmospheric pressure showed that the isotope band is also present in this case, and is not seriously confused with lines from the 0.0 sequence.

§ 2. In order to measure the relative intensity of the λ 4737 and λ 4744 bands by photographic photometry, it was necessary first to reduce the intensity of λ 4737 until it is comparable with that of λ 4744. This was done by means of a thinly silvered glass plate placed immediately in front of the slit of the spectrograph, covering half its height. This reducer was prepared by the evaporation of silver in vacuum, and the constancy of its transmission was insured by covering the silver with a thin layer of evaporated quartz. The transmission at λ 4740 was measured on several occasions with consistent results. This was done by exposing two continuous spectra from a calibrated tungsten band-lamp, one through the silvered part, and one through the clear part of the reducer. Two different currents were used in the standard lamp so that the intensities at λ 4740 were of the same order. These were then compared by means of a set of density marks exposed on the same plate by variation of the slit-width, or of the current in the standard lamp. From the calibration of the lamp, the relative intensities at λ 4740 for the two currents mentioned above could then be computed, using the known emission coefficients of tungsten at this wavelength as a function of the temperature. Table 1 gives the results of four of these determinations, to show their consistency.

TABLE 1.

Plate	T_1	T_2	e_1	e_2	I_1/I_2	Transmission
12a	1996	2633	0.470	0.456	1.63	0.0159
13a	2010	2639	0.470	0.456	1.70	0.0166
15a	2050	2733	0.469	0.457	1.64	0.0159
16a	2020	2675	0.469	0.456	1.60	0.0160
						Av. 0.0160 \pm 0.0001

T_1 and T_2 are the true surface temperatures in the two cases, e_1 and e_2 the corresponding emission coefficients, and I_1/I_2 the measured ratio of intensities on the plate. This method was later checked satisfactorily by

¹⁾ R. C. JOHNSON, *Phil. Trans. Roy. Soc.* **226A**, 157, 1927.

varying the slit width, instead of the current, to render the intensities comparable.

The relative intensities of the two bands may be assumed without appreciable error to be given by the ratio of the peak intensities of the band heads. In measuring this ratio, the intensity of λ 4744 and of the background immediately adjacent to it were measured in the unweakened part of the spectrum, and that of λ 4737 in the weakened part, by means of a set of density marks on the same plate. Subtracting the background intensity, one obtains the true intensity (in arbitrary units) of the isotope band, and, multiplying the ratio of this to the intensity of the weakened main band by the transmission factor of the reducer, 0.0160, the true ratio of λ 4744 to λ 4737 is found. This measurement has been made for four different sources, and the results are summarized in Table 2. The plates were taken on spectrographs having a dispersion of about 20 Å per mm. at λ 4740. Care was taken to illuminate the slit uniformly along its height, and otherwise all precautions were taken which are customary in photographic photometry¹).

The principal source of error in these measurements is the presence of a strong background underlying the isotope band. Non-uniformity of this

TABLE 2.

Plate	Source	4744 and background	Background	4737 weakened	4744/4737
18a	Arc. in argon	10.4	5.9	3.38	0.021
20a	Arc. in argon	39.1	22.9	10.6	0.024
17b	Mecker flame	6.9	4.2	2.75	0.016
2c	Mecker flame	9.4	6.0	3.05	0.018
18b	Oxy-gas flame	27.1	21.3	4.20	0.021
3c	Oxy-gas flame	113.	82.	32.0	0.016
28a	Arc. in hydrogen	61.	47.	6.3	0.034

background, and the blending of extraneous lines with the band are partly responsible for the fluctuations in the results. In the case of the arc in hydrogen, which gave an exceptionally high value, it was suspected that unresolved lines belonging to the 0.0 sequence overlapped the isotope head. This was verified by a spectrogram taken in the first order of the 21-foot grating on which two lines, $\lambda\lambda$ 4743.10, 4746.43, whose aggregate intensity was comparable with the isotope head, were clearly resolved.

§ 3. The apparent absence of the C^{13} isotope bands in the carbon arc in air, mentioned by KING and BIRGE, was next investigated by spectro-

¹) ORNSTEIN, MOLL, and BURGER "Objektive Spektralphotometrie". Vieweg, 1932.

grams taken on the 21-ft. grating. Dense exposures of the 1.0 SWAN band in the second order failed to give visible evidence for the presence of λ 4744. Instead, in the region where the isotope head is expected, a strong background of partly unresolved lines appears. These must be mostly high rotation lines of the 0.0 sequence, which is continued strongly through this region, due to the high temperature of the arc in air. By using the reducer mentioned above, it was found that when the main head is made strong enough so that one should expect to observe the isotope head, the background is strong enough to make observation of the latter practically impossible. Examination of microphotometer curves from these plates gave an indication of a slight rise of the background at λ 4744, but no measurement of its intensity could be made.

The fact that the isotope band is easily observed in the carbon arc in hydrogen, but not in the arc in air, we therefore regard as due to the higher temperature of the latter, which causes the 0.0 sequence to lengthen and cover up the isotope band. Spectrograms of the intermediate condition, *i.e.* of the hydrogen arc containing some air, confirmed this view. These were obtained by forcing jets of hydrogen along each electrode of an open arc, so that the arc burns in an atmosphere of hydrogen contaminated with air. The spectrum shows λ 4744 with apparently the same intensity, but badly confused with higher rotation lines of the 0.0 sequence.

A somewhat more favorable case for finding evidences of C^{13} in the arc in air is the 0.0 band of CN , λ 3883, which is so intense in this source that there are no difficulties with the background. The doublets of the P branch of the 0.0 $C^{13}N$ band, observed by KING and BIRGE in the furnace spectrum, should have half of the intensity, relative to the main lines, given by 4744/4737, remembering that the $C^{12}C^{13}$ molecule has double weight. From the results of Table 2, we should therefore expect them to have a relative intensity of about one percent. However, it was found that the strongest ghosts have an intensity of about 4 percent in the second order of the grating. With the numerous strong lines, and the intense head at λ 3870.4 in the neighbourhood, as well as the existence of higher order ghosts, proof of the presence of $C^{13}N$ lines becomes difficult. To avoid the presence of ghosts, we photographed only a small range of wave-lengths in the interesting region, by using a small glass spectrograph as a monochromator ¹⁾. The desired portion of the λ 3883 band in the prism spectrum was projected on the slit of the grating, and by varying the slit width of the monochromator, the correct range of wave-lengths could be selected. Strong exposures were obtained of the wave-length range $\lambda\lambda$ 3873 to 3877, which includes the lines $P(53)$ to $P(59)$ of the main 0.0 band. The positions where the isotope doublets are expected, on the long wave-length side of the main lines $P(56)$ to $P(58)$ were then free from any possibility of ghosts. The microphotometer curves showed, however, the unmistakable

¹⁾ We are indebted to Mr. H. BRINKMAN for suggesting this procedure

presence of the isotope lines, although they were too faint for a reliable measurement of their intensity.

Discussion.

The results of Table 2 show at once the impossibility of any large dependence of the relative intensity of the isotope band on the temperature of the source. The MECKER flame, which certainly has a much lower temperature than the arc in hydrogen, actually gives a somewhat smaller intensity for the isotope band. However, the evidence points to an equality of intensity, within experimental error, in the four sources investigated. In this event, it would be surprising if the furnace spectrum gives an appreciably different value, unless some self-reversal of the main band occurs. This, however, would cause the intensity of λ 4744 to be higher, rather than lower as indicated by KING and BIRGE in their estimate of 0.005. This figure was obtained by assuming the reciprocity law, adjusting exposure times to make the main and isotope bands of equal intensity, as judged visually. A factor of two was then introduced to allow for the presence of the background in the longer exposure. The same procedure was used by HERZBERG in estimating the relative intensity of the $N^{14}N^{15}$ bands. HERZBERG obtained a value almost three times as small as that found by MURPHY and UREY by quantitative measurements. The application of the reciprocity law is practically certain to yield too small a value, since the exponent in SCHWARZCHILD's law is almost always less than unity. If it has the value 0.9, the error is already 40 percent.

The experiments of § 3 indicate that the isotope band may be present in the arc in air, but that this source is merely an unfavorable case for observing it. Considering the evidence given by KING and BIRGE for the absence of λ 4744 in the arc in air, this rests chiefly on the fact that arc exposures in which the lines of the *P* branch at some distance beyond the head are matched in intensity visually with the corresponding lines in furnace exposures do not show the λ 4744 head nor the lines of this band, even though some of these would lie in positions which are apparently clear of extraneous lines. This is illustrated by enlargements (Plate XII of their paper), in which the furnace and arc spectra are adjacent. Assuming that the *P* lines are exactly matched in intensity, the band head should be much less intense in the arc exposure, because of the higher temperature. This appears to be the case, visually, and a large difference in the intensity of the heads may exist, because a visible difference in blackening indicates, in the range of large densities, a considerable intensity difference. Another factor tending to favour the isotope band in the furnace spectrum is the underlying continuous spectrum. This overcomes the inertia of the plate, bringing faint lines up on the rising part of the density curve. These two factors together seem capable of accounting for the result, although it is

also possible that some self-reversal of the main band in the furnace spectrum also favours the isotopic band.

If the values of the relative intensity we have obtained represent a true measure of the relative abundance, we may compute the resulting atomic weight of carbon. Averaging the data in the last column of Table 2, and omitting the value from the arc in hydrogen for reasons stated above, one finds 0.019. This gives 0.0095, or one part in 106, for the relative abundance of C^{13} atoms. ASTON found 12.0036 for the mass of the C^{12} isotope, which becomes 12.0010 when reduced to the chemical scale. There is no doubt that the C^{13} isotope has a mass of nearly 13, but its exact value is unimportant for our present purpose. With an abundance of one to 106, this would give an atomic weight of 12.010, a value definitely higher than the chemical determinations, which range from 12.000 to 12.006. The discrepancy is similar to those found in the cases of boron and lithium, in that for both of these the rarer isotope has a greater abundance spectroscopically than predicted from the chemical atomic weight.

As already mentioned, our measurements indicate that the relative intensity of the $C^{12}C^{13}$ band is the same in the four sources studied. We find no evidence against assuming that bands due to C^{13} will appear with a corresponding intensity in all other sources. They have not yet been observed in any emission bands of CO or CH , but here the difficulty of the presence of ghosts, when adequate dispersion is used, would be the same as we encountered in the CN band. Finally, as regards the very high intensity of the λ 4744 C_2 band observed in N -type stars, the enormous optical path is certainly adequate to account for this, since the spectrograms show that the main band is completely absorbed to a considerable distance from the head. The same effect is also probably responsible for the surprisingly high intensity of the $C^{13}O$ absorption bands.

In conclusion, we wish to thank Dr. G. O. LANGSTROTH for valuable assistance in the experimental work.

Summary.

The relative intensity of the 1.0 band of $C^{12}C^{13}$ to that of $C^{12}C^{12}$ is measured by photographic methods in four different sources, and found to be effectively constant, its most probable value being 0.019 ± 0.002 . Reasons are given why the isotope band is not observed in the carbon arc in air. The presence of lines due to $C^{13}N$ in the λ 3883 CN band from the arc in air is established. The above intensity ratio corresponds to an abundance of 1 to 106, giving an atomic weight definitely higher than the accepted chemical value.
