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Nuclear Spins of the Carbon Isotopes

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High dispersion spectrograms of the Swan bands of diatomic carbon are obtained from samples enriched to 50 percent and 40 percent, respectively, in C^{13} and C^{14} . The method of exciting an intense spectrum with microgram samples is described. To permit measurements of the alternating-intensity ratio, current densities in the source had to be limited so that the Λ -type doublets were well resolved. For C^{13} , photometric measurements of this ratio give 3:1, showing that the nuclear spin $I = \frac{1}{2}$. The antisymmetric rotational levels have the higher statistical weight (Fermi-Dirac statistics). For C^{14} , only the lines from symmetric levels appear. This shows clearly that $I=0$ for C^{14} , and that the nucleus obeys Einstein-Bose statistics. Wave numbers are given of lines in the R branches of the 0,0 band in the range $K=12$ to 20, due to all molecular species containing C^{12} , C^{13} and C^{14} . An isotope effect in the splittings of the electronic triplets is investigated, and found to agree with that calculated from the general term formula for ${}^3\Pi$ states.

1. INTRODUCTION

BECAUSE of the considerable interest in the spin of C^{14} from the standpoint of the theory of beta-decay, work was begun by the author in the fall of 1946 to develop a technique of determining it when sufficient quantities of this radioactive isotope should become available. These preliminary experiments were carried on with C^{13} , for which the spin determination was then in an unsatisfactory state. The only attempt to measure it, made by Townes and Smythe,¹ had shown that it was either $\frac{1}{2}$ or $\frac{3}{2}$, and the evidence rather favored the latter value. The first result of this work was the proof² that $I = \frac{1}{2}$ for C^{13} . Later it was shown³ that $I=0$ for C^{14} . The

purpose of this paper is to present the details of the two determinations.

Of the two methods of measuring nuclear spins by optical spectroscopy, that using hyperfine structure is most effective for the heavier elements, while that using alternating intensities in band spectra has thus far been the only feasible one for the lighter ones. This is because the light elements have smaller hyperfine splittings, and their lines have a greater Doppler broadening. Hence in the work of Townes and Smythe on C^{13} , it was logical to study the alternating intensities in the well-known Swan bands of diatomic carbon, C_2 . This particular band system is not ideal for such observations, since it is of the rather complex type ${}^3\Pi$, ${}^3\Pi$. The intensity ratio to be measured is in this case the ratio of the two components in a set of narrow doublets, the so-called Λ -doublets. In the C_2

¹ C. H. Townes and W. R. Smythe, Phys. Rev. 56, 1210 (1939).

² F. A. Jenkins, Phys. Rev. 72, 169(A) (1947).

³ F. A. Jenkins, Phys. Rev. 73, 639 (1948).

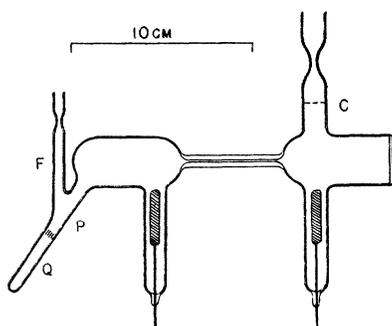


FIG. 1. Discharge tube.

bands, these have a separation of only 0.04Å in the region where they are easily observable, and hence high resolving power is required. Townes and Smythe achieved ample instrumental resolving power by crossing a Lummer-Gehrcke plate with a large grating. This system was so wasteful of light, however, that they were obliged to run their source at large current densities; with a consequent increase in the intrinsic width of the lines. Therefore the Λ -doublets were not resolved in their work.

In the present investigation the method was essentially the same as that of Townes and Smythe, the chief improvement being the use of an excellent Wood grating. This is particularly bright in the second order green, where it has the same resolving power as the Lummer plate mentioned above. The saving of light permitted smaller currents in the source, and the Λ -doublets could then be resolved. Considerable study was also made of the best way of exciting the spectrum with very small amounts of carbon. It was first shown by R. C. Johnson⁴ that a very intense source of the Swan bands is obtained in a sealed-off discharge tube of the conventional type containing about 20 mm of argon or helium, a trace of hydrogen, and small quantities of carbon or of any carbon-containing gas. This method of excitation was used by Wooldridge and the author⁵ in measuring the enrichment of C^{13} in certain samples, and later by Brosi and Harkins.⁶ The present work shows that it is an extremely efficient process, approaching in sensitivity that

⁴R. C. Johnson, *Phil. Trans. Roy. Soc. London* **A226**, 157 (1926).

⁵D. E. Wooldridge and F. A. Jenkins, *Phys. Rev.* **49**, 404 (1936).

⁶A. R. Brosi and W. D. Harkins, *Phys. Rev.* **52**, 472 (1937).

of the best methods of spectrographic detection of metals.

As regards the availability of samples of carbon enriched in the heavy isotopes, the author was fortunate at the outset in having several samples of methane enriched in C^{13} left over from a previous investigation,⁵ and later he obtained some having a concentration as high as 35 percent of C^{13} through the kindness of Professor Smythe. Other concentrated samples of methane were later furnished through the good offices of Drs. A. V. Grosse and W. F. Libby, and finally a sizeable sample of $BaCO_3$ containing 52.5 percent of C^{13} became available. The latter is being used by Dr. Amos Newton of the University of California Radiation Laboratory for the determination of its enrichment in C^{14} , the sample having been produced at the Eastman Kodak Company. Besides these samples enriched by diffusion methods, others were used consisting of microgram amounts of elemental C^{13} separated in the large mass-spectrograph of the Radiation Laboratory, since it was thought that a similar separation of C^{14} from pile-bombarded materials might prove to be the most expeditious method. For the preparation of these samples of C^{13} , and later ones of C^{14} , the author is indebted to Drs. B. J. Moyer and W. L. Whitson. Recently, several milligrams of highly enriched C^{14} prepared by Norris and Snell⁷ were made available through the Isotopes Division of the Atomic Energy Commission.

The spin of C^{13} was first definitely established using the samples from Professor Smythe, while the result for C^{14} was first obtained with the material from Norris and Snell. The mass-spectrographic samples, however, yielded as good a result a few days later.

2. EXPERIMENTAL PROCEDURE

The type of spectrum tube used in exciting the C_2 bands is shown in Fig. 1. It has solid aluminum electrodes, a 1 mm glass capillary, and a fused-on plane glass window. After being filled as described below, the tube was sealed off from the vacuum system, and would usually provide an intense source for many hours. The side-tube *P, Q*, of glass joined to a short piece of quartz

⁷L. D. Norris and A. H. Snell, *Phys. Rev.* **73**, 254 (1948).

tubing Q by a graded seal, was required only when BaCO_3 was the starting material.

The first step in the preparation of a tube was the thorough removal of all impurities of ordinary carbon. This was accomplished by running the tube alternately with air and argon and by an occasional heating of all parts of the tube with a torch to near the softening point. If after filling with pure argon at 20 mm, the head of the green Swan band at $\lambda 5165$ did not appear after 10 minutes' running at a current of 45 ma, the tube was judged to be clean.

Carbon was next deposited on the electrodes, either by decomposition of CH_4 or CO_2 with a discharge, or by slipping over one of the electrodes a cylinder of aluminum foil on which a film of carbon had been collected in the mass-spectrograph. When methane was used, it could be almost completely decomposed at a pressure of a few mm in half an hour. With CO_2 the process was very slow but could be greatly accelerated by adding an excess of hydrogen. When the original sample was in the form of BaCO_3 , it was decomposed thermally in the quartz tube Q by heating the sample introduced through the filling tube F , with a torch to 1100°C .⁸ When the deposit from the mass-spectrograph was used, the connecting tube was cracked off at the point C , the aluminum cylinder slipped over the electrode with forceps, and the tube re-sealed and evacuated prior to adding the argon.

To obtain high intensity of the Swan bands, it is essential that there be the proper amount of hydrogen in the tube, besides the carbon and argon. Apparently hydrocarbons must be formed in the discharge, and their subsequent decomposition gives the C_2 molecules. In the method here used, the necessary hydrogen is evolved from the aluminum electrodes, and could be controlled to some extent by the intensity of the discharge, which determines the heating of the electrodes. Too much hydrogen quenches the bands, and the tubes prepared by inserting aluminum foil were not as satisfactory, because the foil could not be adequately outgassed before sealing off. Mercury must of course be excluded, and this was done by using traps cooled in liquid

nitrogen, or in dry ice and acetone when working with CO_2 .

Some tests of the sensitivity of this mode of excitation were first made by introducing known, small amounts of ordinary CO_2 . Although the ultimate limit of detection was not definitely established, it cannot lie far below $0.07 \mu\text{g}$, with which amount the Swan bands were still obtained strong enough to yield a grating spectrogram. Several micrograms are required, however, to develop the bands to their full intensity, under which conditions the discharge in the capillary is an intense greenish-white color.

The spectrograph utilized a 21 foot aluminum-on-glass concave grating, ruled 30,000 lines to the inch for $5\frac{1}{4}$ in. Its dispersion was $0.568\text{\AA}/\text{mm}$ in the second order. The theoretical resolving power of 315,000 was somewhat greater than that needed for lines of the intrinsic width given by these tubes when they were excited by a current of 45 ma directly from a 20-kv transformer regulated by a rheostat in the primary. Exposures were from 10 minutes to 1 hour on Eastman "Experimental 2a-J" plates, which were kindly prepared at the author's request. These plates showed less fog and finer grain than the 103a-J plates first tried, though their sensitivity at $\lambda 5600$ was about the same.

To permit the measurement of line intensities, the interesting portion of the 0,0 band, $\lambda\lambda 5130-5142$, was photographed through a step-weakener having eight steps 1.5 mm wide, of sputtered platinum on a crystal quartz plate. This was placed, with its steps perpendicular to the spectrum lines, immediately in front of the photographic plate. The astigmatism of the grating was large enough to give lines whose intensity was constant over the greater part of their height. The weakener was calibrated by measuring transmissions for the principal mercury lines with a photocell. Plate densities were measured with a Zeiss recording microphotometer. Relative intensities were always measured by the parallel displacement of the transmission curves, i/i_0 , for each line along the $\log I$ axis.⁹ This method of plate calibration automatically corrects for the most common errors in photographic photometry.

⁸ L. D. Norris and M. G. Inghram, *Phys. Rev.* **73**, 350 (1948).

⁹ Ornstein, Moll, and Burger, *Objektive Spektralphotometrie* (Vieweg, Braunschweig, Germany, 1932), pp. 46, 89.

3. SPECTROGRAMS

No attempt was made to photograph and measure all the lines of the band systems because of the isotopic molecules $C^{12}C^{13}$, $C^{13}C^{13}$, $C^{12}C^{14}$ and $C^{14}C^{14}$. (These molecular species will for convenience be designated 12-13, 13-13, 12-14 and 14-14.) Since the primary interest was in finding the spins, attention was focused on that part of the band systems where the Λ -doublets are most easily observed. This proved to be the same as that selected by Townes and Smythe, namely the R branches of the 0,0 bands between rotational quantum numbers $K=12$ and 20. In this region the isotope shifts and the spacing of successive triplets of the R branch are fortunately so related that there is very little trouble with coincidence of lines of the several isotopic systems.

The advantage of observing this particular region will be clear from Fig. 2, in which the lower strip is enlarged $1.8\times$ from the original plate, and the upper three, $11.1\times$. The isotope

shifts, which here are primarily rotational isotope effects, place the important lines, those of 13-13 and 14-14, in favorable positions for observation. Higher rotational quantum numbers would show larger splittings of the Λ -doublets, but unfortunately the second band of the sequence, the 1,1 band, begins just beyond $R(19)$. At values of K below about 12, there is more confusion of the lines of the different molecules, and the Λ -doublets become too narrow to be resolved.

As will be seen in Fig. 2, the lines of 12-12 and 14-14 show no Λ -doubling. They are, however, alternately displaced toward higher and lower frequency from a smooth series by an amount equal to the Λ -doubling observed for the corresponding unsymmetrical 12-13 and 12-14 molecules. This effect may easily be seen on the spectrograms, since the doubling is negligible for the R_2 lines, and largest for R_3 . Thus the spacing between the central and right-hand components of the electronic triplets is alternately wider and narrower. This "staggering" of the position of

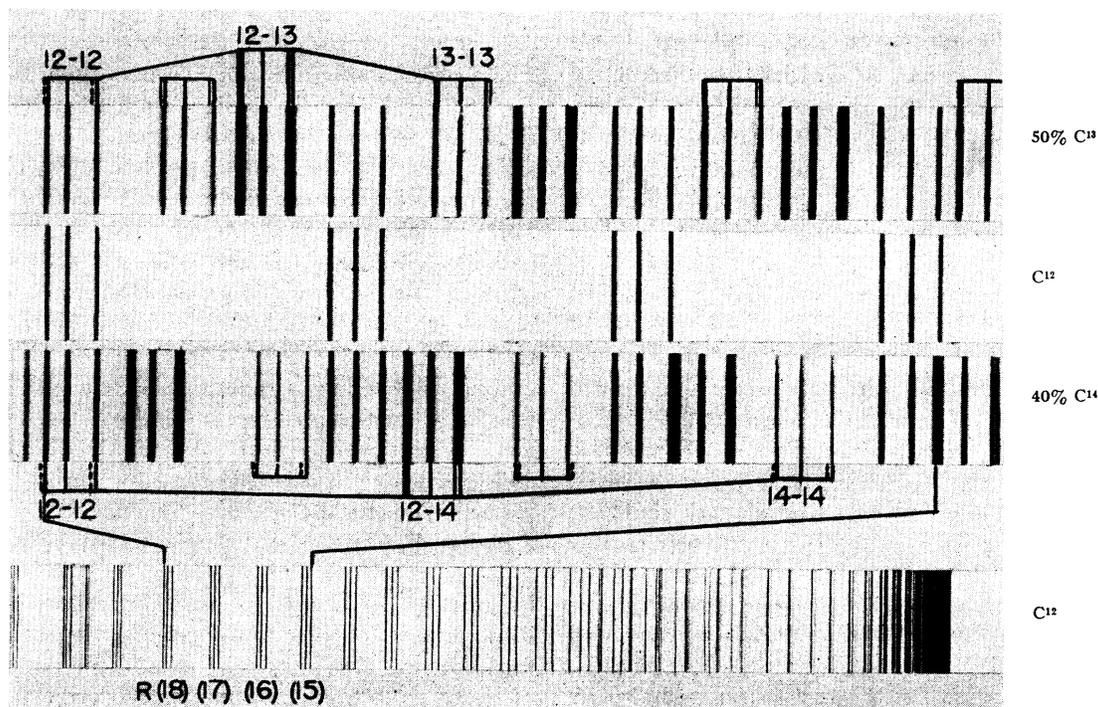
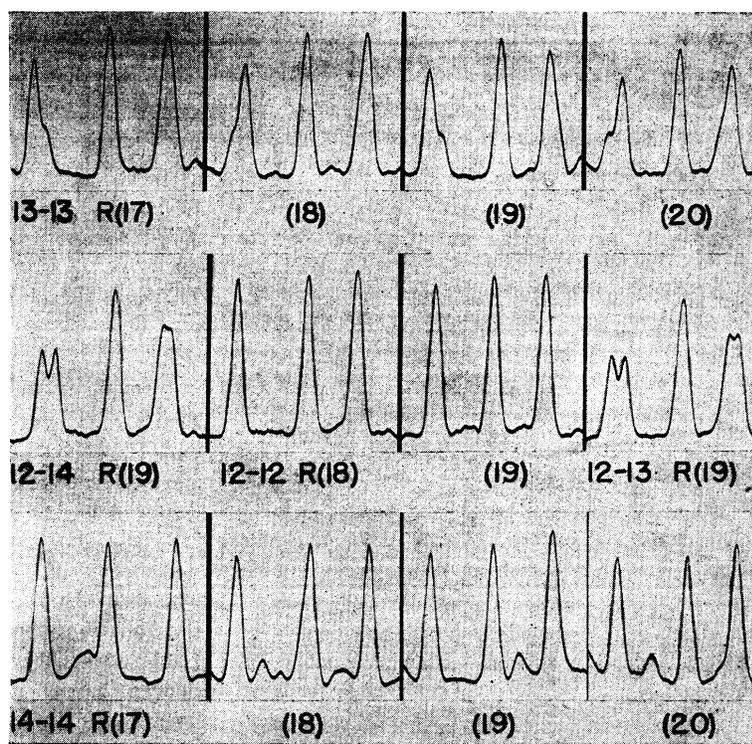


FIG. 2. Spectrograms of ordinary and isotopic carbon. Below is shown the complete 0,0 band of ordinary carbon. The middle of the upper three strips shows four triplets from this band greatly enlarged, while above and below, on the same scale, are the corresponding regions containing the bands due to carbon enriched in C^{13} and C^{14} , respectively. Triplets of the same K value in bands due to the three isotopic molecules have their leaders connected. Other triplets of the heaviest molecule are also marked with short leaders.

FIG. 3. Microphotometer traces of triplets of the R branch. Top, due to $C^{13}C^{13}$; middle, $C^{13}C^{12}$ and mixed molecules; bottom, $C^{14}C^{14}$.



the lines is well-known¹⁰ in the ordinary Swan bands, and results from the fact that alternately one component and the other of the Λ -doublets is missing because the nuclear spin is zero. The 13-13 bands, on the other hand, show both components, with different intensities. This is a characteristic of the finite nuclear spin.

Three sets of plates were studied intensively. First, a set in which the measured intensities indicated a concentration of 33 percent C^{13} in the spectrum tube, which was made from the best Smythe sample. The lines of 12-13 and 13-13 were identified on these plates, and a detailed analysis made of the intensity contours of three of the R_3 Λ -doublets of 13-13. These indicated an intensity ratio of 3:1, and, since this ratio of the statistical weights is $(I+1)/I$, where I is the nuclear spin, the latter was reported² to be $\frac{1}{2}$ for C^{13} . The second set was made using the best sample of C^{14} from Norris and Snell, and showed 40 percent C^{14} . The complete absence of one component of the Λ -doublets was obvious on inspection, and therefore it was concluded³ that $I=0$ for C^{14} . The last set was

¹⁰ J. D. Shea, Phys. Rev. 30, 825 (1927).

made with the richer C^{13} material from the Eastman Kodak Co., and permitted a measurement of the intensity ratio for eight doublets, the results of which agree with the previous conclusion, as will be shown below.

The first plates showed clear resolution of the Λ -doublets of R_3 in 12-13. This may be seen in the microphotometer curves shown in Fig. 3. The left-hand component of the triplet for $R(19)$ (center strip, at the right) has a measured splitting of 0.041 \AA . That this is considerably greater than the theoretical limit of resolution of the grating, 0.0163 \AA , proves the chief cause of the observed width of the lines to be in the light source, and not in the grating. In Fig. 3, it will be seen that there is even a beginning of resolution of the $R_1(19)$ doublet. The separation of this doublet as predicted from the "staggering" of the R_1 lines of the 12-12 bands (see below) is only 0.021 \AA .

Since some interest may attach to the values of the isotope shifts from the standpoint of the theory of this effect in $^3\Pi$, $^3\Pi$ bands, the wavenumbers of all lines measured are given in Table I. These data are obviously very incomplete,

TABLE I. Wave-numbers of lines caused by various isotopic molecules.

K''	J''	12-12	12-13	13-13	12-14	14-14
11	(R_2)	19,435.13 <i>S</i>	19,431.58	19,428.06 <i>S</i>	19,428.54	19,421.84 <i>S</i>
		— <i>A</i>	31.73	28.17 <i>A</i>	28.69	— <i>A</i>
12	12(R_2)	36.15 <i>S</i>	32.60	29.04 <i>S</i>	29.59	22.87 <i>S</i>
		— <i>A</i>	32.60	29.04 <i>A</i>	29.59	— <i>A</i>
	13(R_1)	37.13 <i>S</i>	33.67	30.15 <i>S</i>	30.66	24.00 <i>S</i>
		— <i>A</i>	33.67	30.15 <i>A</i>	30.66	— <i>A</i>
	12	— <i>A</i>	37.81	33.99 <i>A</i>	34.55	— <i>A</i>
		41.77 <i>S</i>	37.97	34.13 <i>S</i>	34.71	27.55 <i>S</i>
13	13	— <i>A</i>	38.79	34.99 <i>A</i>	35.54	— <i>A</i>
		42.57 <i>S</i>	38.79	34.99 <i>S</i>	35.54	28.45 <i>S</i>
	14	— <i>A</i>	39.75	35.95 <i>A</i>	36.52	— <i>A</i>
		43.50 <i>S</i>	39.75	35.95 <i>S</i>	36.52	29.51 <i>S</i>
	13	48.29 <i>S</i>	44.27	40.21 <i>S</i>	40.80	33.17 <i>S</i>
		— <i>A</i>	44.41	40.35 <i>A</i>	40.95	— <i>A</i>
14	14	49.19 <i>S</i>	43.20	41.14 <i>S</i>	41.77	34.15 <i>S</i>
		— <i>A</i>	43.20	41.14 <i>A</i>	41.77	— <i>A</i>
	15	49.93* <i>S</i>	46.06	42.03 <i>S</i>	42.57	35.12 <i>S</i>
		— <i>A</i>	46.06	42.03 <i>A</i>	42.57	— <i>A</i>
	14	—	50.93	46.61	47.24	—
		55.38	51.08	46.74	47.38	39.27
15	15	—	51.83	47.51	48.13	—
		56.13	51.83	47.51	48.13	40.07
	16	—	52.60	48.29	48.94	—
		56.89	52.60	48.29	48.94	40.95
	15	62.41	57.83	53.25	53.90	45.27
		—	57.97	53.38	54.04	—
16	16	63.22	58.68	54.10	54.76	46.17
		—	58.68	54.10	54.76	—
	17	63.88	59.39	54.87	55.52	46.93
		—	59.39	54.87	55.52	—
	16	—	64.94	60.06	60.77	—
		69.93	65.08	60.19	60.91	51.80
17	17	—	65.76	60.88	61.60	—
		70.64	65.76	60.88	61.60	52.52
	18	—	66.40	61.51	62.24	—
		71.28	66.40	61.51	62.24	53.26
	17	77.41	72.27	67.12	67.85	58.20
		—	72.43	67.25	68.01	—
18	18	78.18	73.07	67.92	68.65	59.01
		—	73.07	67.92	68.65	—
	19	78.70	73.60	68.57	69.28	59.64
		—	73.71	68.57	69.28	—
	18	—	79.84	74.35	75.16	—
		85.25*	80.01	74.51	75.31	65.08
19	19	—	80.63	75.14	75.94	—
		86.07	80.63	75.14	75.94	66.76
	20	—	81.12	75.66	76.46	—
		86.64	81.22	76.66	76.55	66.40
	19	93.40	87.61	81.86	82.70	71.89
		—	87.77	82.02	82.85	—
20	20	94.08	88.18	82.64	83.47	72.65
		—	88.18	82.64	83.47	—
	21	94.64	88.76	83.22	83.93	73.19
		—	88.76	83.22	84.04	—

* Values from Shea (reference 10) appeared to be in error. More exact values are 19,450.01 and 19,485.46 cm^{-1} .

and could be greatly extended by further work on the plates. In the wave-length measurements, the iron arc standards were not used; instead the accurate wave-lengths of the 12-12 lines given by Shea¹⁰ were used as reference lines. This was done partly for convenience, partly with the idea that since the shifts are more significant than the absolute values, wave-lengths measured relative to those of Shea would be most useful.

In Table I, *S* and *A* designate the symmetric and antisymmetric character of the wave func-

tions of the states involved, exclusive of the part due to nuclear spin. Thus, in the upper electronic state, ${}^3\Pi_\rho$, the *S* states are those with + rotational functions,¹¹ and the *A* with - ones, whereas in the lower, ${}^3\Pi_u$, the correlation is *S* with -, and *A* with +. In both 12-12 and 14-14 the *A* states and lines are missing while in 13-13 the lines involving *A* states are considerably stronger than those involving *S* states. This will be further discussed below.

4. SPIN OF C^{13}

Identification of the lines due to 12-13 and 13-13 was easy when plates were compared which showed different concentrations of the heavier isotope. As a check, however, the shifts were calculated by the approximate relation

$$\Delta\nu = (\rho - 1)\nu_v + (\rho^2 - 1)\nu_r, \quad (1)$$

where $\rho = (\mu_1/\mu_2)^{1/2}\nu_v$ and ν_r were evaluated by the aid of the constants for 12-12 as given by King and Birge.¹² This gave shifts about 2.5 percent larger than the observed ones. For example, the line $R_2(18)$ of 12-13 is expected to have a vibrational shift of -1.40 cm^{-1} and a rotational shift of -3.88 cm^{-1} , total -5.28 . The observed shift was -5.12 cm^{-1} . The origin of this discrepancy lies in the fact that the electronic and rotational energies are not properly separated by this method (see below). In predicting the shifts for other isotopic species, however, quite accurate results were obtained by assuming the calculated vibrational shift to be correct and applying rotational shifts proportional to $\rho^2 - 1$ relative to the observed rotational shift for 12-13.

The relative intensities of the bands due to 12-12, 12-13 and 13-13 are in the ratio $1:2r:r^2$, where r is the ratio of the numbers of atoms of C^{13} and C^{12} . From each plate, r was determined by measuring the relative intensity of several corresponding R_2 lines in the three bands. (These lines were chosen because they have a negligible Λ -doubling.) It was found that tubes prepared from the 35 percent material gave intensities corresponding to $r = 0.5$, or a concentration of 33 percent, while those from the 52.5 percent sample gave 49 percent. This slight

¹¹ R. S. Milliken, Rev. Mod. Phys. 2, 146 (1930).

¹² A. S. King and R. T. Birge, Astrophys. J. 72, 38 (1930).

reduction from the initial concentrations resulted from unavoidable contamination with traces of ordinary carbon. When the amount of the sample was only a few micrograms, as with the mass-spectrograph deposits, this effect was more important. Even though these deposits must have consisted essentially of the pure single isotope, the greatest precautions had to be taken in order to obtain in this way a tube exhibiting a concentration higher than 30 percent of the heavier isotope.

For the measurement of the spin, the R_3 doublets were used since these have the widest splitting. Even for them, however, there was rarely an appreciable minimum between the two components because of the large difference in their intensities. The weaker component usually appeared merely as a shoulder on the side of the stronger one (see the left-hand component in upper strip of microphotometer traces in Fig. 3). In measuring the intensity ratio, two other difficulties exist, besides the lack of clear resolution. One is the presence of a number of weak lines of extraneous origin, some of which may coincide with the lines to be measured. Certain of these are the weak P branches returning from the band heads, but the most disturbing ones appear to be due to impurities, for example CN which will appear if any nitrogen is present. It was evidently the presence of a weak line of CN lying just on the short wavelength side of the line $R_3(19)$ that led Townes and Smythe to favor the higher value of the spin; it caused a spurious width for the weaker component. The other difficulty is the existence of a continuous background, which even on the best plates contributed about one-third the intensity of the weaker line. This line itself has only one-fourth of the total intensity of the R_3 doublet, which in 50 percent material is only one-half as strong as the unresolved R_2 doublet of 12-13. Hence the background is only 1/24 or 4 percent as intense as the strongest lines. Measuring it accurately, however, was one of the chief difficulties.

Since all of the three effects mentioned (lack of resolution, spurious lines, and background) tend to reduce the measured ratio of peak intensities below the true value, the following method was adopted. The peak intensities of the two components, the weaker of which was actually more of

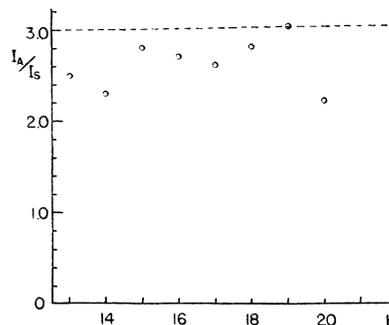


FIG. 4. Measured intensity ratios of the components of the A -doublets in $C^{13}C^{13}$.

a shoulder than a peak, were measured for eight R_3 doublets of 13-13 and the intensity of the background subtracted from each. The ratio of the values for the two components were then plotted against rotational quantum number, as shown in Fig. 4 for the plate taken with 49 percent C^{13} . This should reveal the effect of spurious lines by large fluctuations, and the effect of lack of resolution by a decreasing ratio at lower rotational quantum numbers where the splittings are less. Both these effects are to be seen in Fig. 4. That the lines $R_3(14)$ and $R_3(20)$ have disturbing lines superposed on the weaker component was verified by examining other plates taken with a smaller concentration of C^{13} . It is clear, however, that the ratio approaches at large K the theoretical value of 3.0 for a spin $I = \frac{1}{2}$. The next higher possible spin, $I = \frac{3}{2}$, would give an intensity ratio of 1.67, in definite disagreement with these measurements.

These results appear to definitely establish that the spin of C^{13} is $\frac{1}{2}$. Although the exact value taken for the background has an important influence on the intensity ratios, it should be emphasized that no possible choice of background will bring the ratio down to 1.67. Without subtracting any background at all, the measured ratios are still about 2.0. Furthermore, a proof that there are no serious errors in the photometry is given by the fact that the intensities of corresponding R_2 lines of 12-12, 12-13 and 13-13 in the 50 percent sample came out very close to the theoretical values 1:2:1.

As regards the statistics obeyed by the C^{13} nucleus, it was concluded by Townes and Smythe,¹ and is verified here, that the A lines are the stronger, as required for Fermi-Dirac statistics. This may be seen directly in either

Fig. 2 or Fig. 3 from the circumstance that for lines of the same rotational quantum number the component which is missing in 12-12 is the one which is the stronger in 12-13. The nucleus of C^{12} since it contains an even number of particles, obeys the Einstein-Bose statistics.

5. SPIN OF C^{14}

Band lines caused by C^{14} were first obtained with a tube containing a $2.7 \mu\text{g}$ deposit from the mass-spectrograph. Unavoidable contamination with ordinary carbon, however, resulted in an intensity of the 12-14 band corresponding to only 16 percent of C^{14} . This was sufficient to show lines due to 14-14, but they were so weak that it was difficult to identify them with any certainty among the many weak impurity lines. Shortly thereafter, a 2.6 mg sample of BaCO_3 furnished by Norris and Snell,⁷ and reported to have¹³ a concentration of approximately 19 percent, was tried. It was actually much richer than this, since the intensity measurements yielded 27 percent C^{14} . On these plates the 14-14

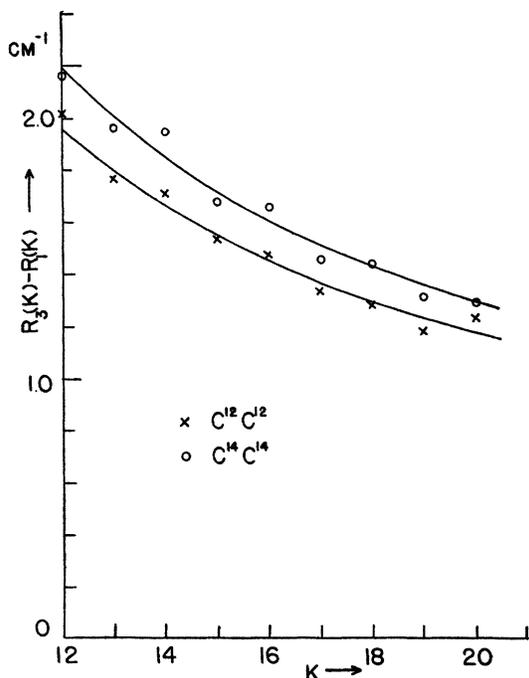


FIG. 5. Observed and calculated widths of the spin triplets.

¹³ The author is informed by Mr. Norris that a corrected count on this sample gave the figure 22 percent. Similarly, the second sample used here should have been 32 percent instead of 27 percent. See L. D. Norris, *Bull. Am. Phys. Soc.* **23**, 46 (1948), paper T9.

lines were plainly visible, and a comparison with the previous plates left no doubt as to their correct identification, since all of the true lines were about four times as strong. No doubling whatever of these lines could be detected, although the resolution was at least as good as on the C^{13} plates. Furthermore, a staggering of the R_3 lines was apparent, and it therefore seemed clear that the spin of C^{14} is zero as in C^{12} .

Two further sets of plates were obtained showing still higher concentrations of C^{14} , one with a sample supposed¹³ to contain about 27 percent of C^{14} , and another with a $5.8 \mu\text{g}$ sample from the mass-spectrograph. Photometric measurements on the first set, from which Figs. 2 and 3 were made, showed 40 percent C^{14} . The mass-spectrographic sample was split in two, and half put on each electrode. This, combined with extreme precautions to avoid contamination by ordinary carbon, resulted in a tube which also showed a concentration of 40 percent. These plates with greater enrichment served to confirm very definitely the results reached earlier. If the spin of C^{14} had been finite, the weaker component of the Λ -doublets would necessarily have been at least $\frac{1}{2}$ (or possibly $\frac{1}{3}$) the intensity of the stronger one, and could not conceivably have been overlooked. The 14-14 lines on these plates are nearly half as strong as those due to 12-12.

The statistics of the C^{14} nucleus is, as expected for a nucleus with an even number of particles, the same as for C^{12} , i.e., Bose-Einstein. This is determined from the fact that for lines of the same rotational quantum number, the staggering is in the same direction. Examination of Figs. 2 and 3, particularly a comparison of the lower two strips in Fig. 3, will show the definiteness of this effect.

6. ISOTOPE EFFECT

A more exact calculation of the isotope shifts than is given by Eq. (1) could be made with the aid of the theoretical term formulas for $^3\Pi$ states given by Budó.¹⁴ In this paper are to be found also the rotational and electronic constants of the 0,0 band of C_2 , upon which Budó tested the theory. Since there is now little reason to doubt the correctness of this theory, the complete calculations have not been made here. One feature of the observed shifts, however, is

¹⁴ A. Budó, *Zeits. f. Physik* **98**, 437 (1935).

apparent from inspection of the plates, and can easily be compared with theory. This is the fact that the width of the spin triplets is not the same for lines of the different isotopic molecules having the same rotational quantum number. It increases with the mass of the molecule, and in 14-14 is some 10 percent greater than in 12-12. This effect may be seen in Fig. 2, and especially in Fig. 3, where the triplets $R(18)$ and $R(19)$ are placed one above the other for 12-12 and 14-14.

If the triplet splittings were purely electronic in origin, they would be the same for different isotopes, but it is well known that in multiplet electronic states there is an interaction between electronic and rotational motion. Hence for the correct evaluation of the effect of mass on these splittings, one must utilize the theoretical term formulas. In the present case a simplification results from the fact that in the range of rotational energies involved the spin is almost completely uncoupled from the molecular axis (case b coupling). With the assumption that the rotational energy is large compared to the multiplet splitting, one can show from Budó's equations that the over-all width of the triple levels, or the splitting of the levels $F_3(J=K-1)$ and $F_1(J=K+1)$ reduces to

$$F_3(K) - F_1(K) = \frac{BY(Y-4)}{4} \left(\frac{1}{K-\frac{1}{2}} + \frac{1}{K+\frac{3}{2}} \right). \quad (2)$$

Here $Y=A/B$ has the values -10.4 and -9.4 in the lower and upper states. Two isotopic species will have values of B in the ratio ρ^2 , and of Y in the ratio $1/\rho^2$. Hence the splitting should involve a factor somewhat less than $1/\rho^2$. This is found to be the case.

Figure 5 is a plot of the measured triplet widths in the observed range of K values. The solid curves show the theoretical variation according to Eq. (2). The actual calculations, using the constants given by Budó, gave both of these curves 0.36 cm^{-1} lower, but this is because the line splittings are the differences between two much larger term splittings, and hence are very sensitive to the exact values of the constants. For comparison purposes, the computed values were therefore increased 0.36 cm^{-1} . The ratios between the line separations for 12-12 and 14-14 are in satisfactory agreement with theory, averaging 0.903 as compared to the computed 0.905. ρ^2 is 0.857. The scatter of the points in

Fig. 5 is largely due to the staggering, which makes the splittings for even K larger than those for odd K .

7. DISCUSSION

The two values of the spin here determined, $I=\frac{1}{2}$ for C^{13} and 0 for C^{14} are definite, and consistent on the basis of comparison with the spins of known stable nuclei, but the latter value poses serious difficulties to the accepted theory of beta-decay. The half-life of C^{14} 5100 years, and the energy of its beta-rays, 155 kev, place it on the third Sargent curve so that the transition is at least twice forbidden. Therefore a large spin change is expected by the Gamov-Teller selection rules, but is not observed since the transition is $I=0 \rightarrow 1$.

No attempt will be made here to discuss possible explanations of this discrepancy. It is briefly treated in a forthcoming publication by A. Roberts,¹⁵ who concludes that his observations on the microwave spectrum of OCS are consistent with $I=0$ for C^{14} .

It should be emphasized that the band spectrum method of determining nuclear spins is the only method that gives a positive result in cases where $I=0$, since in all other methods a vanishing magnetic moment or electric quadrupole moment, will give a null result regardless of the value of I . The success of the present experiment is an indication that the method may find other similar applications among stable or artificially radioactive isotopes that can only be obtained in small quantities.

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¹⁵ A. Roberts, Phys. Rev. **73**, 1405 (1948).

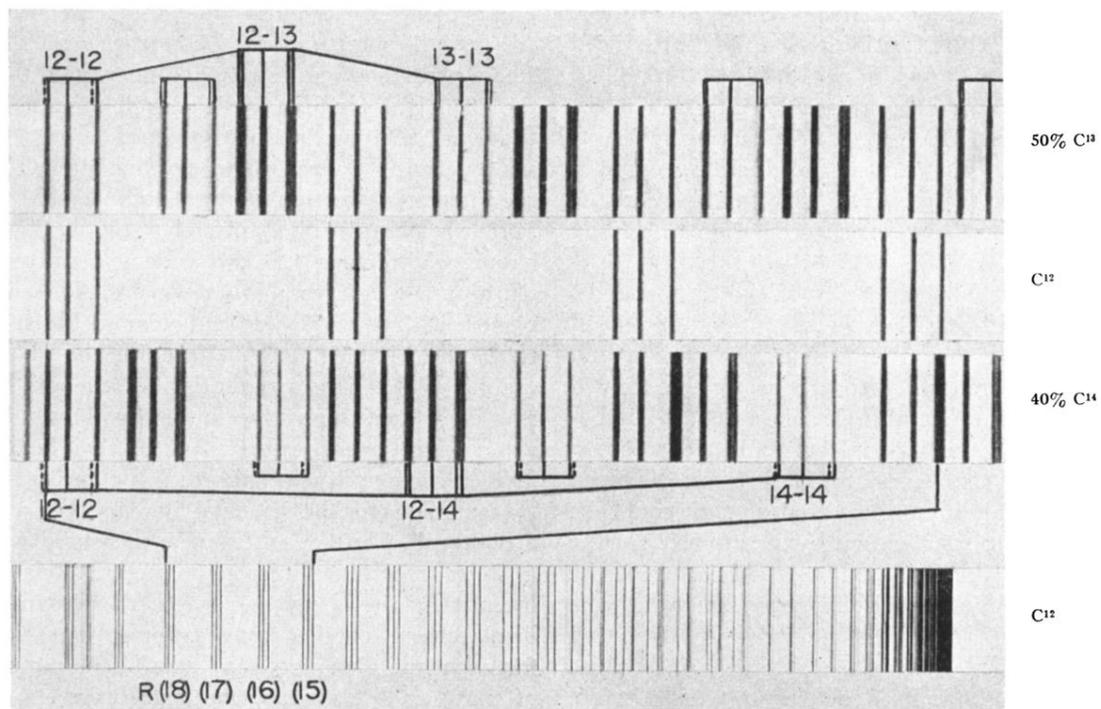


FIG. 2. Spectrograms of ordinary and isotopic carbon. Below is shown the complete 0,0 band of ordinary carbon. The middle of the upper three strips shows four triplets from this band greatly enlarged, while above and below, on the same scale, are the corresponding regions containing the bands due to carbon enriched in C¹³ and C¹⁴, respectively. Triplets of the same K value in bands due to the three isotopic molecules have their leaders connected. Other triplets of the heaviest molecule are also marked with short leaders.

FIG. 3. Microphotometer traces of triplets of the *R* branch. Top, due to $C^{13}C^{13}$; middle, $C^{12}C^{12}$ and mixed molecules; bottom, $C^{14}C^{14}$.

