

CONCENTRATION OF THE HEAVY ISOTOPE OF CARBON
AND MEASUREMENT OF ITS NUCLEAR SPIN

Thesis by
Charles H. Townes

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Abstract

Heavy carbon was concentrated with a Hertz diffusion apparatus to a maximum of 50%, and enough carbon at 30 to 40% concentration was obtained to make possible spectroscopic and nuclear disintegration work. The concentration was in two processes. Ordinary methane was let continuously through the light reservoir of a Hertz apparatus for the collection of a large quantity of gas containing 6 or 7% heavy methane, then this gas reintroduced into the system for a final concentration. Measurements on the $C^{13}-C^{13}$ band spectrum show that the C^{13} nucleus obeys Fermi-Dirac statistics and probably has a spin of $1/2$. A 21 ft. grating and Lummer-Gehrke plate combined were used to resolve the close Λ -type doublets of the $O-O$ (λ 5165) band of the $C^{13}-C^{13}$ Swan system. Resolution was not complete, but was enough to determine the nuclear statistics and allow a good estimate of the spin. Further proposed work with the concentrated heavy carbon is outlined and some conclusions drawn from isotopic effects in an unidentified band which has hitherto been assigned to the carbon molecule.

Part I. Concentration of Carbon Thirteen

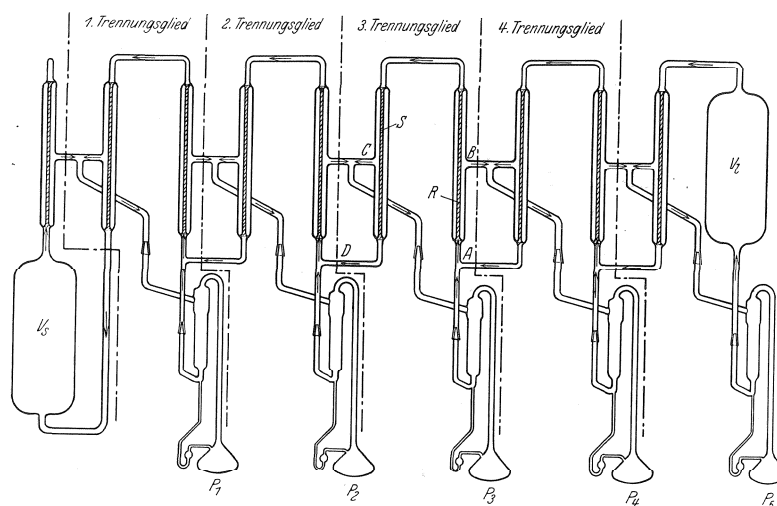
General Discussion of Hertz' Apparatus

Although separation of isotopes by means of their different rates of diffusion was one of the most obvious and first tried methods, it was not until Hertz developed his apparatus allowing the convenient exchange of gas between a series of diffusion stages that this became a practical method of concentrating some of the rare isotopes enough for physical measurements. Hertz' apparatus has proved most successful in the separation of isotopes of the rare gases neon and argon, and of carbon.

Qualitatively, the operation of this diffusion apparatus may be seen from separation member (Trennungsglied) 3 of plate I. The lightest parts of the gas which flows into porous tubings R and S in the direction indicated by arrows diffuses through their walls and is taken by mercury diffusion pumps P_3 or P_4 . The gas which reaches the opposite ends of R and S is, then, heavier than that which enters. Separation member 3 thus receives heavy gas from member 4 at A and returns light gas at B, while at corresponding points C and D it receives the lightest fractions of gas from member 2, and passes on its own heavy gas. In this way heavy isotopes are moved toward reservoir V_3 and light isotopes toward reservoir V_1 until a steady state is reached.

With certain simplifying assumptions, the most significant of which are listed below, it is not difficult to find that when a steady

Plate I



Hertz' Diagram of his Diffusion Apparatus

V_1 - Reservoir for heavy gas

V_2 - Reservoir for light gas

R and S - Porous tubes

state is reached, the separation factor

$$Q = \left[\frac{f^\mu}{1 - (1 - f)^\mu} \right]^n, \text{ where}$$

$$Q = \frac{c_s}{c_l} = \frac{\text{ratio of heavy to light molecules in } V_s}{\text{ratio of heavy to light molecules in } V_l}$$

$$\frac{1}{f} = 2 + \frac{\text{length of tube S}}{\text{length of tube R}}$$

$$\mu = \frac{\text{mass of light molecule}}{\text{mass of heavy molecule}}$$

n = number of separation member

under the assumptions

1. The gas consists of a mixture of two isotopes
2. Diffusion along the tube is negligible
3. The pressure is zero outside of the porous tubes
4. The pressure is sufficiently low that viscosity effects are negligible.

For the usual case where a high concentration of the heavy isotope is desired, the above formula shows that c_l and n should be as large, f and μ as small as possible. Breakdown of assumption 2 and consequently of the formula for Q with small f limits its value rather fundamentally to about $1/15$, while practical considerations, discussed by Wooldridge¹, make n less than about 50. Thirty four diffusion members, designed and built by Wooldridge, having f between $1/10$ and $1/20$, were used in the present work to separate methane

¹ Thesis, C. I. T., 1936.

containing C^{13} from methane containing C^{12} , so that $c_s \approx 40 c_\ell$ theoretically. Methane gas was of course chosen for the separation of C^{13} because it afforded a larger fractional difference in molecular weight or a smaller μ than any other carbon containing gas. Values of c_ℓ must now be considered.

Ordinarily, gas containing a mixture of isotopes is let into the Hertz apparatus and diffused, enriched gas being taken out of V_s when a steady state is nearly reached. In this case, if V_ℓ has a large volume compared to the volume of the rest of the apparatus, c_ℓ is approximately equal to the isotopic concentration of the gas originally let in; but if V_ℓ is not sufficiently large, its supply of heavy molecules may be appreciably depleted for the enrichment of gas in V_s and the separation members near V_s . If, for example, gas containing a normal concentration c_0 of heavy isotope is let into the system and diffused, the enriched gas will have a concentration considerably less than Qc_0 , where Q is the separation factor, unless the volume V_ℓ is much larger than the volume of the remaining parts of the apparatus, or in particular than V_s .

Also, if gas which has undergone preliminary enrichment is let into the system, a rather large amount is required to fill the necessarily large volume V_ℓ .

Statement of the Problem of Separation

Wooldridge obtained methane containing 10% C^{13} by diffusing ordinary methane in a 35-member apparatus with a 22 liter bulb for V_ℓ

and a 500 c.c. bulb as V_S . By saving the concentrated gas from several runs and reintroducing it into the diffusion system with a quantity of ordinary methane, he collected a small amount of 16% heavy methane. With this heavy carbon, Jenkins determined the mass ratio of C^{13} and C^{12} . It seemed desirable to produce more concentrated C^{13} for spectroscopic~~al~~ measurement of its nuclear mechanical and magnetic moments, and also to produce a large enough quantity of reasonably concentrated C^{13} to use for nuclear disintegration study.

Measurements of the band spectra of the $C^{13}-C^{13}$ molecule, which, as shown below, was the most promising method of determining the C^{13} nuclear spin, was also most demanding on the concentration of C^{13} . It is easily seen that, if there are n_{12} atoms of C^{12} and n_{13} atoms of C^{13} per unit volume, then the relative abundance of molecular $C^{12}-C^{12}$, $C^{12}-C^{13}$, and $C^{13}-C^{13}$ is $n_{12}^2:2n_{12}n_{13}:n_{13}^2$, assuming the carbon atoms combine at random. This means that the intensity of radiation from the $C^{13}-C^{13}$ molecule in such a mixture is $\left[\frac{n_{13}}{n_{12} + n_{13}}\right]^2$ of the total radiation of carbon molecules, or is proportional to the square of the percent C^{13} , so that a mixture of 30% or more C^{13} must be obtained to make this measurement feasible.

If the abundance of the heavy isotope in V_g were kept at its normal value of about 0.7%, a theoretical maximum of but 22% C^{13} could be obtained in V_S , so that a preliminary enrichment of a large enough quantity of methane to fill the system was evidently needed. To collect a few hundred c.c. of methane at 1 cm pressure containing 50 - 75%

$C^{13}H_4$, about 150 times as much gas as had heretofore been collected in a one-day run at about one-half the maximum concentration obtained was needed, so that a rather different technique and much more labor was called for.

Experimental Procedure

Rather than using a reservoir of several hundred liters for V_L in order to prevent an appreciable change in c_L during the collection of a large quantity of enriched gas, the methane in V_L was continually renewed during the diffusion. A large tank of very pure methane was obtained with the help of Dr. B. H. Sage from a natural gas well. This gas was let consecutively through a pressure regulator, stopcock, and the walls of a small porcelain tube into V_L , which contained about 1 cm of methane. Gas was removed from another part of V_L through the walls of a larger porous porcelain tube, another stopcock, and a pumping system. With this arrangement, the pressure in V_L could be easily controlled by the pressure regulator on the methane tank. When the pressure regulator was set, it was not disturbed during a run, so that the gas could be continually renewed in V_L , or, by turning both the stopcocks mentioned above, renewed periodically without disturbing the pressure in V_L or the process of diffusion.

With this arrangement for making V_L effectively infinite, and a 500 c.c. bulb for V_S , the enrichment of methane was determined for various pressures and times of diffusion. When the methane pressure in V_L rose above 9 mm., the maximum enrichment obtained was somewhat

decreased, probably because of the breakdown of assumption 3 above, that pressure outside the porous tubes is zero. But during operation a pressure gradient along the diffusion system exists which makes the pressure in V_3 about 3 mm. when there is 9 mm. pressure in V_2 , so that a rather small quantity of methane is collected. The system was found to operate with reasonable efficiency when the pressure was as high as 14 mm. in V_1 , or 8 mm. in V_3 , yielding 10 to ~~12~~ % $C^{13}H_4$ in the 500 c.c. bulb after about 10 hrs. diffusion. The richest methane, produced with lower pressure, was 14 or 15% $C^{13}H_4$ giving $Q \approx 23$, considerably short of the theoretical $Q = 40$. Wooldridge attributed his failure to approach the theoretical enrichment to the finiteness of V_2 , and could explain his results by assuming an "effective volume" for each separation member of about 110 c.c. This work with an "infinite" volume for V_2 shows that failure to obtain the theoretical enrichment is rather due to the inaccuracy of the assumptions under which the theoretical formula was derived, and that the "effective volume" of the separation members is probably simply the measured volume of about 60 c.c.

Enrichments were determined largely from the relative intensities of the $C^{12}-C^{13}$ 1,0 (λ 4744.5) band head and the $C^{12}-C^{12}$ 1,0 (λ 4737.1) head of the Swan system. These bands were produced with considerable intensity in a capillary discharge tube containing about 1 cm. pressure of argon and a trace of methane, activated by a 20,000 volt transformer. A Hilger E I glass spectrograph gave suitable

dispersion for intensity measurement. Plate II provides a picture of these bands with several concentrations of C^{13} .

With the operating characteristics of the diffusion system determined, a 5 l/2 liter container was put in V_S for a preliminary enrichment of methane. If the separation members have negligible volume and are considered only as a means of interchanging light and heavy molecules between V_S and V_L , it is evident that the time of diffusion required to obtain a given enrichment in V_S is directly proportional to the volume of V_S . It was expected, therefore, that this enlarged V_S would contain gas of about 10% heavy methane after four or five days diffusion, and spectra from small samples of gas removed during diffusion showed this to be correct.

At the end of a five-day run, the apparatus usually required reconditioning in several respects. Invariably mercury ~~distilled~~ from the diffusion pumps and clogged the tubing through which gas circulated. Sometimes this mercury demanded removal before a run was completed. For this and other possible trouble during a diffusion run, connections were made so that the 5 l/2 liter bulb could be cut off, air let into the system, the mercury removed, and diffusion begun again with only a 500 c.c. bulb as V_S . When the concentration in this bulb reached its value before diffusion was interrupted, circulation of a gas through the 5 l/2 liter bulb was begun again. Four successful runs of four or five days were made with the 5 l/2 liter bulb in V_S , the gas in this bulb showing about 10% heavy methane in each case. Gas was collected

each time not only from V_S , but from the nearby separation members which also contained enriched methane, so that in all, nearly twenty-five liters of gas at a centimeter pressure was obtained for a re-diffusion. This gas, however, contained something like 20% impurities.

Small quantities of heavy foreign gases were a serious menace in this experiment, for the diffusion apparatus concentrates all heavy gas into V_S , and if the gas is appreciably heavier than methane, this concentration is very efficient. Although the system usually seemed quite tight, there were undoubtedly small leaks which let in noticeable quantities of air over a period of four or five days. Some carbon monoxide and dioxide was given off by the hot glassware and by stopcock grease, although greased stopcocks were replaced in most cases by mercury valves. An unavoidable source of impurities was the methane gas used. It was more than 99.5% pure, with the impurities largely CO , CO_2 , and N_2 . But since this gas flowed through V_L at the rate of about 3 liters at a centimeter pressure per minute, the total amount of impurities provided was quite large. To minimize this source, for some of the diffusion runs fresh methane was not let through V_L continuously, but for fifteen minutes every two hours. The presence of CO_2 and H_2O caused very little trouble, for they were removed simply by a liquid air trap on one of the tubes connecting V_S to the diffusion system. Oxygen seemed to combine slowly with the methane so that it appeared

as carbon oxides and water. This was expected because the presence of the mercury green line near the jets of the diffusion pumps indicated a source, probably electrostatic, of energies above 7 e.v. The most bothersome foreign gases requiring removal were, then, nitrogen, carbon monoxide, and a small quantity of argon.

The carbon monoxide was oxidized with iodine pentoxide, and the resulting carbon dioxide and free iodine produced according to the equation $5 \text{ CO} + \text{I}_2\text{O}_5 \rightarrow 5 \text{ CO}_2 + \text{I}_2$ frozen out in the liquid air trap mentioned above for the removal of CO_2 . A tube containing a small quantity of iodine pentoxide was put in the system so that gas passed through it directly into the liquid air trap, and then into V_S , since it was this gas near V_S which contained the largest quantity of CO. By keeping the I_2O_5 at 150° C with an oil bath, carbon monoxide was almost completely oxidized, while the I_2O_5 did not itself decompose or react with the methane appreciably.

The nitrogen, because of its inertness, could not be removed by chemical means without at the same time destroying the methane with which it was mixed. After some attempts at combining it at low temperatures with calcium and barium amalgams, it was decided that the difference in vapour pressures of nitrogen and methane at liquid air temperatures afforded the best means of separation of these two gases. Nitrogen is, of course, near atmospheric pressure at liquid air temperatures, while methane has a vapour pressure 1.9 cm at -192° C (liquid air) and 5.5 cm. at -184° C (liquid oxygen). Nitrogen was not removed

during diffusion as were the other foreign gases, but after the preliminary diffusion had been made, when, as mentioned above, it was about 20% of the collected gas. This gas was compressed by a Töppler pump into a 100 c.c. bulb with a small projecting tube dipped in freshly made liquid air. The methane was then a liquid near its freezing point (-184°C) in the bottom of the tube, excepting about 5 centimeters pressure in the 100 c.c. bulb, while the nitrogen was a gas in the bulb at about 70 centimeters pressure. A large stopcock from the 100 c.c. bulb into an evacuated 5 liter bulb was then suddenly opened and closed. The nitrogen of course rushed into the larger bulb, while very little methane had time to evaporate and flow into the larger bulb. All the gas was recompressed into the 100 c.c. bulb and expanded suddenly into the larger bulb several times until it was sure a minimum of methane was lost with the nitrogen. Preliminary tests with mixtures of methane and air showed that not more than $1/15$ of the methane was lost. Practically all of the nitrogen and the small quantity of argon present was eliminated, making the enriched methane ready for a final diffusion.

During diffusion, the collected gas produced a pressure of 7 mm. in the 22-liter V_L , and in V_S , a 500 c.c. bulb, a pressure of 2 mm. The abundance of heavy methane was measured just before diffusion was begun to be 6 or 7%. Three runs of about 10 hours were made and the gas collected and tested, showing a maximum abundance of 50% heavy methane. This gives a separation factor $Q \approx 19$ for the

apparatus, in agreement with the value 23 found earlier. The 5 1/2 liter bulb was then connected with V_S , and a 45-hour run made to collect a large quantity of gas of medium enrichment before discarding the gas remaining in V_g and the separation members.

Results

The approximate quantities and analyses of the various enriched samples of gas obtained are as follows:

Sample number	<u>Quantity of methane at 1 cm. pressure</u>		<u>Percent C ¹³ H₄</u>
I	100 c.c.		25
II	10 c.c.		50
III	175 c.c.		40
IV	900 c.c.		30

Part II. Measurement of the Spin of Carbon Thirteen

Probably the most important physical quantities which may be measured with sufficiently concentrated carbon thirteen are the spin and magnetic moments of the C^{13} nucleus. Of the three methods of making this measurement which have been successful in other cases - deflection of molecular beams in an inhomogeneous field, measurement of hyperfine structure, and measurement of relative intensities in alternate band lines - the last two seemed most promising, so were considered in detail.

Method of Hyperfine Structure

Hyperfine structure in atomic spectral lines is due to the energy of interaction between the magnetic moment of the nucleus and magnetic fields associated with the spin and orbital motions of extranuclear electrons. Because this energy is small compared with other energies which determine the energy levels of an atom, it may be calculated by a perturbation method very similar to that used for the Zeeman effect. The coupling between nucleus and electron is largest for an electron which stays near the nucleus and increases with an increase in the effective nuclear charge. To obtain a hyperfine structure large enough for measurement, therefore, one looks for lines involving a penetrating electron with small total quantum number, preferably in a highly ionized state of the atom. For interferometer measurement of the structure, the lines must also have long

enough wavelength to be well reflected by silver and not absorbed in glass, they must be fairly well isolated from other lines, and must, of course, have a width less than the distance between components of the hyperfine structure.

In the case of carbon the strong triplet of C III $3p^3P - 3s^3S$ ($\lambda\lambda$ 4651.35, 4650.16, 4647.40) seemed most favorable. Using the predicted values for the magnetic moments, the line $3p^3P_2 - 3s^3S$ of this triplet would show 3 components for a spin of $1/2$, and 8 components for a spin of $3/2$, requiring resolution of lines separated by about 0.10 cm. for nuclear moment determination. Unfortunately, the C III line proved difficult to obtain without extreme excitation and consequent large Doppler broadening of the lines. While this hyperfine structure measurement seemed on the horizon of possibility, and had the advantage of determining both the spin and magnetic moment, it was abandoned for the more promising band spectra method of spin measurement.

Method of Band Spectra - Structure of Molecular Spectra

The principal effect which nuclear spin has on band spectra is in producing an alternation in the intensity of the fine structure lines. This was first noted by Mecke in the negative nitrogen bands, and was explained by Heisenberg and Hund in 1927 as a typical quantum mechanical effect of the nuclear spin on the statistical weights of molecular states. In order to construct an appropriate wave-function

and to find the exact role of nuclear spin in band spectroscopy, the nature of molecular states must be investigated.

The coordinates required to specify the condition of a diatomic molecule are :

1. those of its center of mass
2. two angles of orientation
3. the distance between nuclei
4. the positions of all electrons with respect to the center of mass
5. all electron spins
6. the nuclear spins.

If, for a first approximation, the assumption is made that there is negligible energy coupling between these degrees of freedom, or that the generalized forces and masses for one coordinate are unaffected by the values of the other coordinates, the problem of finding the molecular energy may be broken up into a number of simpler problems. Quantum-mechanically, the Hamiltonian and wave functions are then separable and the energies involved in each degree of freedom may be found from solutions of some of the standard quantum-mechanical problems as follows:

Problem	Resulting characteristic energies
1. A free particle	Continuous range
2. A free rotator	$E = \frac{J(J + 1) \hbar^2}{2I}$
	where I = moment of inertia $J = 0, 1, 2, \dots$

- | | |
|--|---|
| <p>3. A simple harmonic oscillator
[assuming a force between
nuclei $k(d - d_0)$ where d is
distance between nuclei and
d_0 the equilibrium distance]</p> | $E_v = (v + \frac{1}{2}) h \sqrt{\frac{k}{m}}$ <p>m = reduced mass of atoms
$v = 0, 1, 2, \dots$</p> |
| <p>4. Electrons in axially symmetric,
or approximately spherically
symmetric electric field.</p> | <p>Energies cannot be calculated
very easily, but are approxi-
mated by electronic energies
in atomic systems.</p> |
| <p>5. Spin coupling of electrons in
orbits.</p> | <p>The number of energy levels
may be found as in the similar
atomic case, but energies can-
not be exactly calculated.</p> |
| <p>6. Magnetic rotators in uniform
field (produced by motion of
electrons).</p> | <p>Number of levels = $(2s + 1)^2$
where s = spin of nucleus
energies very small.</p> |

Fig. 1 indicates the relative magnitudes and spacings of all these energies, excluding that due to translation. The spectra of diatomic molecules provide an excellent verification of this treatment and at the same time give the slight modifications needed to take into account coupling between different degrees of freedom. The most significant of these coupling effects are those due to interacting between electron spin and orbital motion, and between electron orbital motion and rotation of the molecule.

According to the usual rules for quantization of angular momentum, the resultant spin S may have $2S + 1$ different orientations with respect to the orbital momentum Λ about the internuclear axis, giving $2S + 1$ different energies of interaction, or $2S + 1$ components

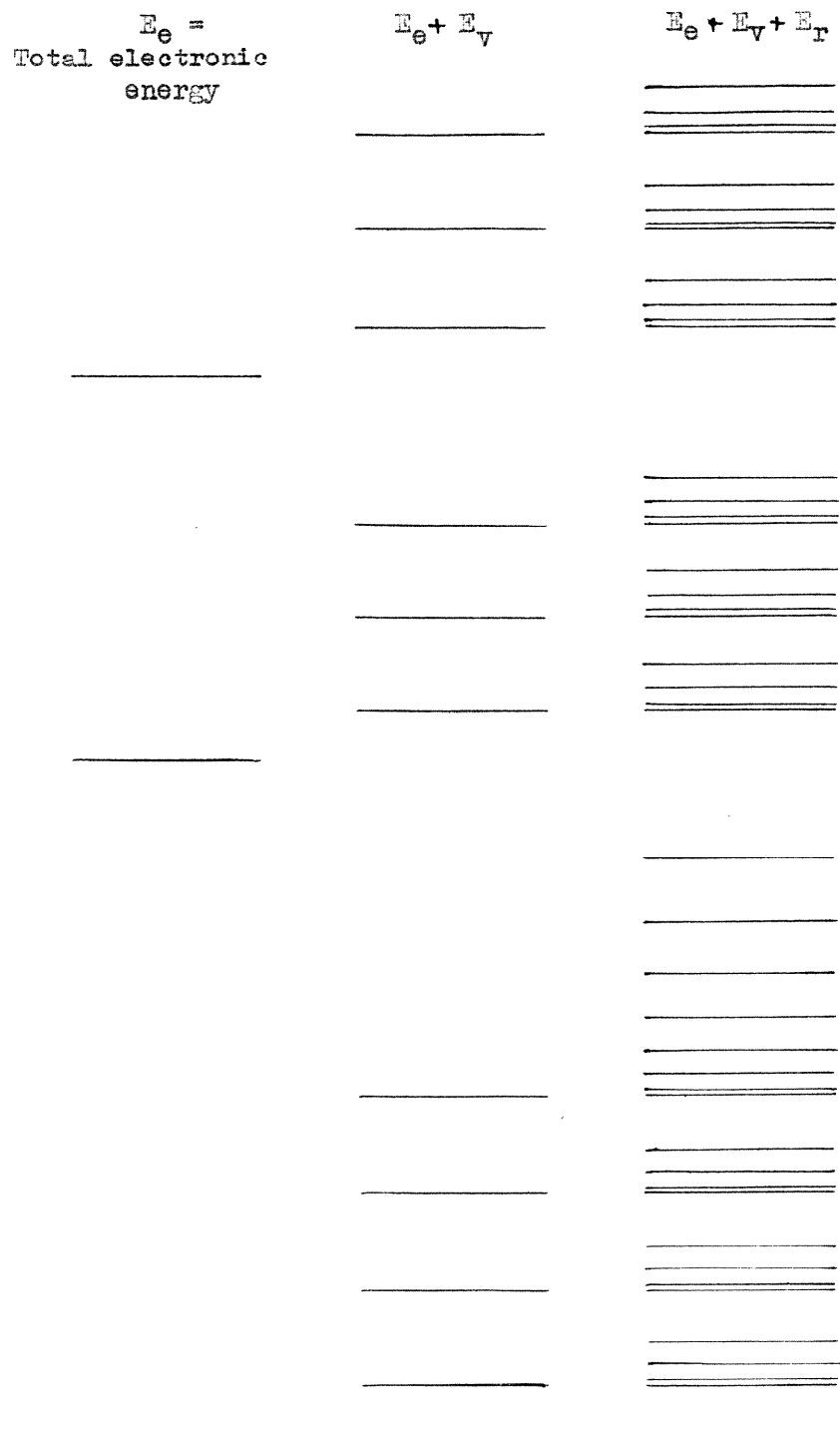


Fig.1

The spacing of the rotational levels should be reduced by a factor of about fifty to give the correct ratio of their spacing to that of the vibrational levels.

of the so-called spin multiplets, somewhat closer, usually, than the different rotational levels. Coupling between electronic orbital momentum and molecular rotation produces two levels for the two different orientations of Λ with respect to the momentum of molecular rotation. This is called Λ -type doubling.

The designation of these levels has been made similar, as far as possible, to atomic level nomenclature. Thus the symbol $^n\chi_m$ indicates a level for which the resultant spin is $\frac{n-1}{2}$, the sum of the components of spin and orbital momentum about the internuclear axis is m , and the component Λ of the orbital momentum about this axis is given by χ . Where for $\chi = \Sigma, \Pi, \Delta$, $\Lambda = 0, 1, 2$ respectively. Vibrational and rotational levels are designated simply by their quantum numbers v and J .

Method of Band Spectra - Nuclear Spin and Symmetry Properties

It is apparently a fundamental law of nature that the quantum-mechanical wave-function of any system must be either symmetrical or antisymmetrical in any two identical particles or entities included in the system. That is,

$$\psi(x_1, x_2, \dots, x_n, \dots, x_s, \dots) = \pm \psi(x_1, x_2, \dots, x_s, \dots, x_n, \dots)$$

if x_n represents all the coordinates of the n^{th} particle, and particles r and s are identical, where the plus sign applies if particles r and s obey Einstein-Bose statistics, the minus sign if they obey Fermi-Dirac statistics. A homonuclear molecule such as

$C^{12} - C^{12}$ or $C^{13} - C^{13}$ is an example, the wave-function being symmetrical or antisymmetrical in the atomic nuclei according to the statistics which they obey. ~~The wave function for a $O - O$ which they obey.~~ The wave-function for a $C^{12} - C^{13}$ molecule, however, is subject to no symmetry requirement.

From the very small interaction between nuclear spin and the other degrees of freedom of a molecule, we can with considerable confidence assume a wave function of the form $\psi = \psi' \psi''(s_a s_b)$ for some homonuclear diatomic molecule, where s_a and s_b are the spin variables for the two nuclei a and b, and ψ' is a function of all the other molecular variables. For ψ to be symmetric with respect to the two nuclei, ψ' and ψ'' must be both symmetric or both antisymmetric; but for ψ to be antisymmetric, one of the factors ψ' and ψ'' must be symmetric, the other antisymmetric. To construct suitable functions ψ'' consider $\psi'' = f(s_a)f(s_b)$. There are $2s + 1$ different independent functions $f(s_a)$, $f_2(s_a)$, ... $f_{2s+1}(s_a)$, corresponding to $2s + 1$ different orientations of the spin s_a with respect to, say, the internuclear axis. Similarly there are $2s + 1$ different independent functions $f(s_b)$, $f_2(s_b)$... $f_{2s+1}(s_b)$, so that in all there are $(2s + 1)^2$ different ψ'' . These must be combined in the proper way to obtain the same number of linearly independent symmetric or antisymmetric functions, since they are the only types which can have physical significance. The desired ψ'' are simply $f_m(s_a) f_n(s_b) \pm f_m(s_b) f_n(s_a)$, where the plus sign makes ψ'' symmetric

with respect to the 2 nuclei or the indices a and b, the minus sign makes it antisymmetric. For $m \neq n$, there are then $(2s + 1)s$ of each type of function; but for $m = n$ the antisymmetric functions disappear, and we have only $2s + 1$ symmetric functions of the form $2f_n(s_a)f_n(s_b)$. If the nuclei obey Fermi-Dirac statistics the final ψ must be antisymmetric, so that a ψ' which is symmetric may be combined with $(2s + 1)s$ antisymmetric ψ'' to give $(2s + 1)s$ levels of slightly different energy, or a single level of statistical weight $(2s + 1)s$, while from a corresponding antisymmetric ψ' , a level of weight $(2s + 1)(s + 1)$ can be made. The ratio of population of the two levels is then
$$\frac{\psi' \text{ sym}}{\psi' \text{ antisym}} = \frac{s}{s + 1}.$$
 For nuclei which obey Einstein-Bose statistics the total ψ must be symmetric, and
$$\frac{\psi' \text{ sym}}{\psi' \text{ antisym}} = \frac{s + 1}{s}.$$
 Now the selection rules for dipole radiation are such that for a transition, the symmetry or antisymmetry of is not changed. In addition, the nuclear spin functions would not be expected to change during a transition because of the small forces acting on the nuclear spins. The result is that spectral lines are divided into two groups of transitions between symmetric ψ' and transitions between antisymmetric ψ' whose relative intensities are multiplied by a factor $\frac{s + 1}{s}$ because of the identity of the two nuclei.

To determine what lines are to be used for a measurement of this effect and the spin S , one must know the symmetry of the ψ' of the levels from which they arise. The function ψ' may be written

$\psi' = G_1(r_1, \dots, r_n) G_2(\Lambda, J) G_3(v) G_4(X)$ where r_n represents all the coordinates of the n^{th} electron, Λ, J and v are the quantum numbers, and X represents the three coordinates of the center of mass. G_1 is symmetrical or antisymmetrical with respect to the nuclei according as the summation $\sum_n l_n$ is even or odd, where l_n is the orbital momentum of the n^{th} electron, and its symmetry is independent of the spin variables. The rotational function G_2 is even or odd for even or odd J for one component of the Λ -type doublet and vice versa for the other component. The other two factors are always symmetrical. The ~~selection~~ ^{selection} rules for dipole radiation require $\Delta \sum l_n = \pm 1$, $\Delta J = \pm 1$, and that the orientation of Λ with respect to J does not change. Therefore both G_1 and G_2 change their symmetry in a transition, but ψ' does not. Symmetric levels are indicated by light lines in Fig. 2a, antisymmetric levels by heavy lines. The resultant variation in intensities of a few lines of the carbon spectrum are shown in Fig. 2b. The lines would normally be very nearly the same intensity as shown by the $C^{12} - C^{13}$ lines. Note that since the spin of the C^{12} nucleus is zero, $\frac{S}{S+1} = 0$, alternate lines are missing entirely.

Experimental Requirements and Technique

For the measurement of this intensity effect, bands produced by Σ states have the distinct advantage of not showing Λ -type doubling ($\Lambda = 0$) so that intensity alternation is displayed by

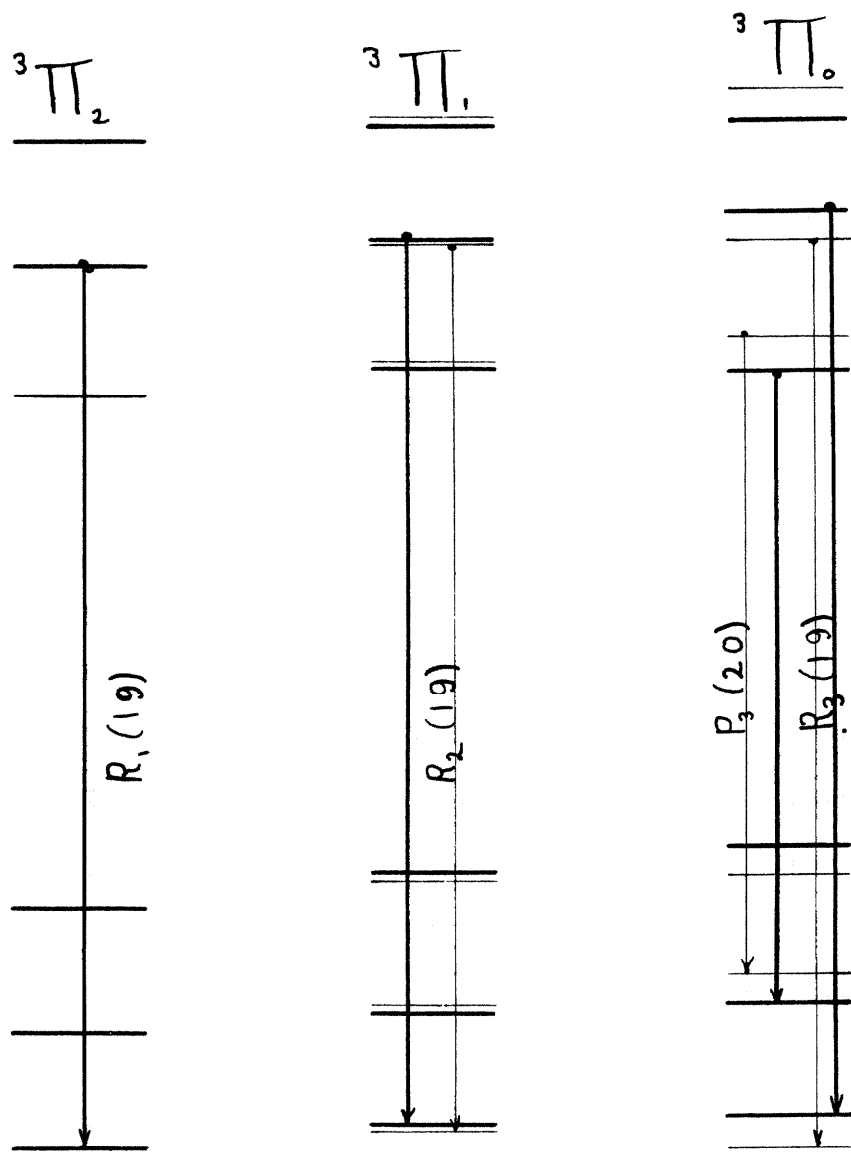


Fig. 2a.

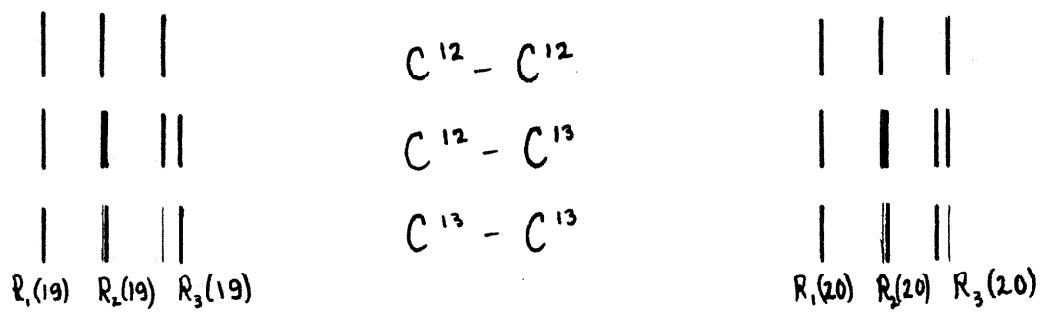


Fig. 2b.

adjacent rotational lines rather than by the close Λ -type doublets. Unfortunately, no Σ band has been found for the carbon molecule.*

The principal bands of C_2 are the Deslandres-d'Azambuja $\pi-\pi'$ and the Swan ${}^3\Pi-{}^3\Pi$ bands. The $\pi-\pi'$ bands seemed at first most favorable, since they had one component to every three of the ${}^3\Pi-{}^3\Pi$

bands, and they showed fairly large Λ -type doubling.

But these bands are usually obtained from the continuous disintegration of a hydro-carbon gas at fairly high pressure in an electrical discharge, and this type of excitation is certainly not feasible with a limited amount of enriched isotopic gas. A number of attempts failed to excite the Deslandres-d'Azambuja bands to any intensity at low pressures, so the Swan bands were turned to and the most promising lines for a measurement of alternating intensities picked out.

In order to make the desired measurement, lines of the $C^{13}-C^{13}$ spectrum must be found showing Λ -type doubling which is wide enough to permit resolution of the two components, and in addition are not covered up or their intensities affected by other nearby lines. This latter requirement eliminated most of the lines of the $C^{13}-C^{13}$ Swan system because they were interfered with by adjacent lines due to the molecules $C^{12}-C^{13}$ and $C^{12}-C^{12}$. If one assumes the same fields of force about and between the carbon nuclei in any of the molecules $C^{12}-C^{12}$, $C^{12}-C^{13}$, and $C^{13}-C^{13}$, then it is seen that the energy levels of these molecules are approximately the same. The principal

* Mulliken mentioned work on a supposed Σ band, but gave no data and there was no subsequent publication on this band.

differences are due to the effect of the different nuclear masses on the vibrational energy $E_v = \hbar \sqrt{\frac{k}{m}} (v + \frac{1}{2})$ where m is the reduced mass, and the rotational energy $E_r = \frac{\hbar^2}{2I} J(J + 1)$, where I is the moment of inertia. This effect puts part of the (1,0) and (2,0) bands of $C^{13}-C^{13}$ clear of the bands produced by the other two molecules, but this part of the bands shows very close doublets. The (0,0) band was chosen as the strongest band of the system, and showing the least interference between spectra of the three molecules.

An examination of the behavior of the triplets and doublets of the R-branch of this band (see Fig. 3) shows two possible places where the desired measurements may be made, in the region of members 70 and 80 where the spin triplets have drawn together and the Λ -type doubling is large, and in the region of members 15 to 30 where the triplet structure is enough larger than the doubling not to interfere and the doubling barely large enough to resolve. Since the doublet structure for members 70 to 80 makes no great requirements on resolving power, a cylindrical lens was used with a 21-ft. grating to give these lines with convenient exposures of 5 to 10 minutes. With ordinary carbon, these lines stood out strongly against the background of lines from other branches; but the increase of background due to the superposition of three band systems of $C^{12}-C^{12}$, $C^{12}-C^{13}$, and $C^{13}-C^{13}$, in addition to the less intensity of the desired lines, made intensity measurement hopeless. The members of the R-branch just before the head of the (1,1) band head, numbers 15 - 20, were much more intense

and had very little background, but required higher resolving power for resolution of the desired components. The R_3 components ($^3\Pi_0 - ^3\Pi_0$) of $C^{12} - C^{12}$ show a "staggering" which indicates a doublet separation of about 0.04 \AA in this region, while the other components show less than 0.02 \AA separations (see Fig. 3). According to theory, if the molecule exhibits Hund's Case a coupling, the component R_3 should show this constant doubling for all members, the component R_2 ($^3\Pi_1 - ^3\Pi_1$) should show splitting proportional to $J(J + 1)$, and the R_1 ($^3\Pi_2 - ^3\Pi_2$) component should show negligible splitting. Case a coupling requires that spin-orbit interaction is much larger than spin-molecular rotation interaction. The measured staggering of $C^{12} - C^{12}$ lines indicate that case a coupling holds fairly well for this molecule for the rotational lines considered, but not for higher members.

The lines under discussion are at about 5200 \AA , so that a resolving power of about 130,000 was required for separation of the two components of R_3 . Since carbon in a discharge tube "cleans up" or disappears rapidly, it was highly important to minimize exposures while obtaining this high resolving power. Unfortunately, none of the gratings and mountings available gave high enough resolving power and dispersion for this purpose. A concave 21-ft. 6-inch grating was found to give just sufficient resolution by examining visually the mercury lines; but when these lines were recorded on a photographic plate, the additional spreading of about 15μ was enough to prevent

Behavior of the R branches of the (0,0) Swan band.

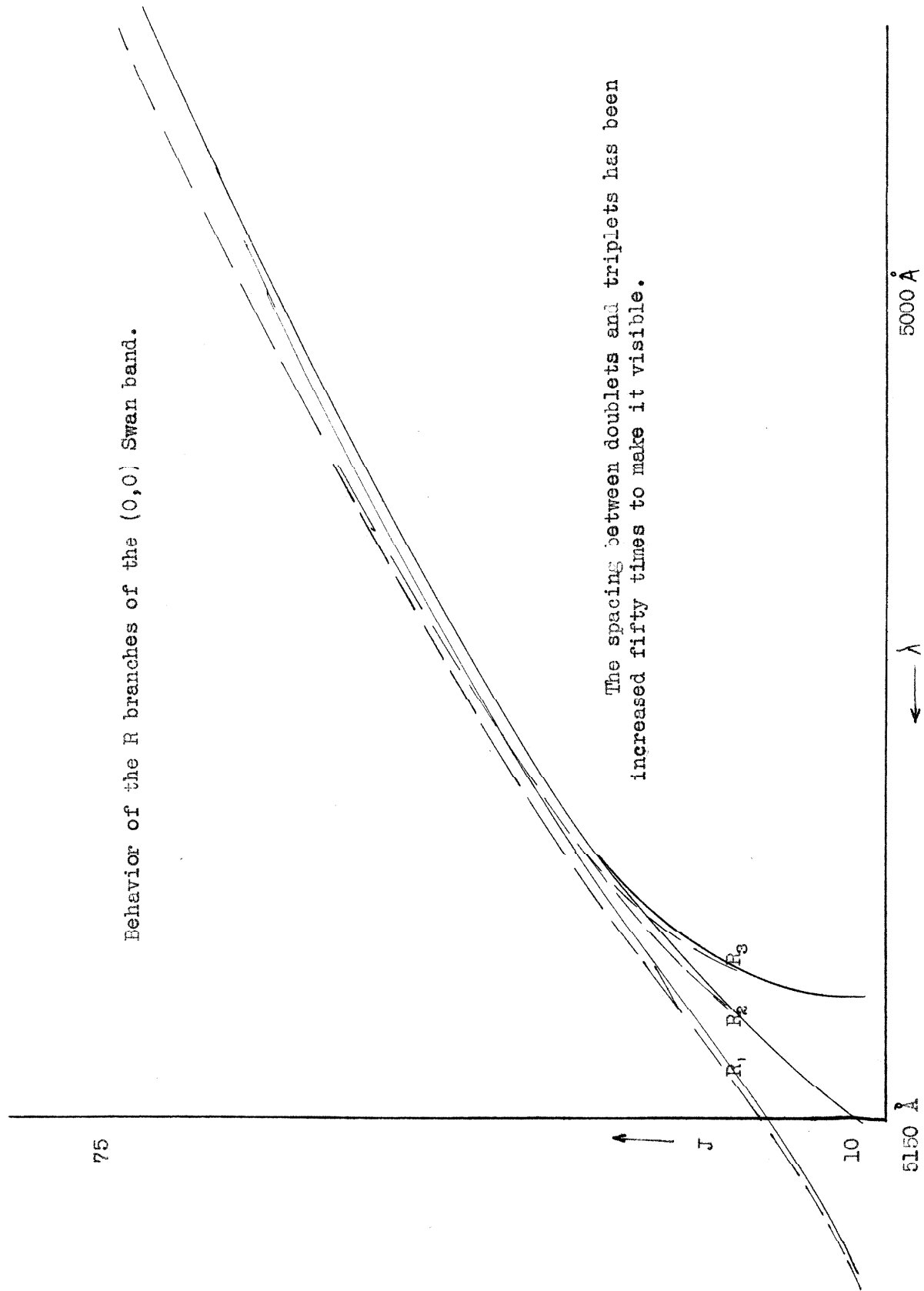


Fig. 8.

resolution. A Fabry-Perot interferometer can provide sufficient resolution, but requires prohibitive exposure times, particularly since it would have to be used in this case with high dispersion for isolation of the desired lines. One of the principle sources of inefficiency of such an interferometer is that to secure high resolution and a reflecting power of, say, 90%, one unavoidably loses 90% of the light available on introducing it into the interferometer. A Lummer-Gehrke plate eliminates this difficulty by utilizing the high reflecting power of glass near the critical angle and letting light into the glass at normal incidence.

To find the resolving power and characteristics of a Lummer plate, consider Fig. 4a and the quantities

t = thickness of plate

i = angle of emergence of light beam

r = angle of reflection of " "

n = order of spectrum

μ = index of refraction of the glass

λ = wavelength of light.

The retardation between consecutive rays is

$$\begin{aligned} n\lambda &= AB + BC - AD = 2t\mu \sec r - 2t \tan r \sin i \\ &= 2t \sqrt{\mu^2 - \sin^2 i} \end{aligned}$$

$$\text{since } \mu \sin r = \sin i$$

Differentiating this expression with respect to n , the angular separation between consecutive orders n and $n + 1$ is

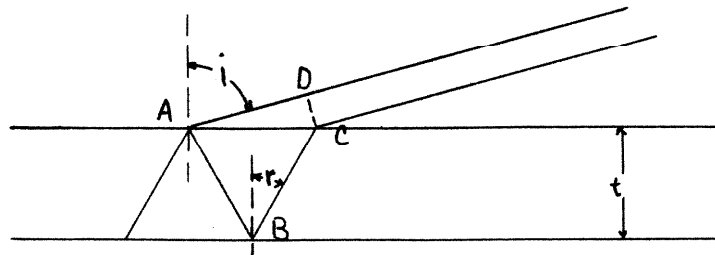


Fig. 4a. Theory of the Lummer Plate

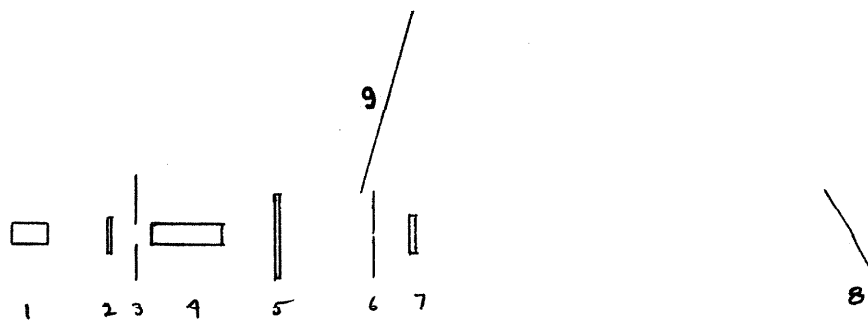


Fig. 4b. The Optical System

1. Capillary source
2. Lens to make light from source parallel
3. Light baffle and aperture
4. Lummer plate
5. lens to focus parallel light on slit
6. Slit
7. Cylindrical lens to correct astigmatism
8. Grating
9. Photographic plate

$$\Delta i = \frac{-\lambda \sqrt{\mu^2 - \sin^2 i}}{t \sin 2i} . \quad \text{Differentiating the same expression}$$

with respect to λ , the dispersion is found to be

$$\frac{\partial i}{\partial \lambda} = \frac{2\lambda \mu \frac{\partial \mu}{\partial \lambda} - 2(\mu^2 - \sin^2 i)}{\lambda \sin 2i} \quad \text{To find the resolving power, we}$$

make the simplifying assumption that every beam emerging from the plate is of equal intensity, so that the angular distance between a position of reinforcement of the beams and the first minimum of the diffraction pattern is $\Delta i = \frac{\lambda}{\ell \cos i}$, since $\ell \cos i$ is the apparent aperture of the plate. Combining this expression with the formula for

$$\text{dispersion, the resolving power } \frac{\lambda}{\Delta \lambda} = \frac{\ell}{\lambda \sin i} (\mu^2 - \sin^2 i - \mu \lambda \frac{\partial \mu}{\partial \lambda})$$

For the plate available, $t = 4.5$ mm. and $\ell = 130$ mm., so that the order of interference $n \approx 18500$ and $\frac{\lambda}{\Delta \lambda} \approx 300,000$ for $i \approx 80^\circ$.

The theoretical resolving power of the plate was therefore sufficient. It was tested visually and photographically by the use of the green mercury line and found actually to give sufficient resolving power and to show no ghosts.

The plate was crossed with a 21 ft. concave Eagle-mounted grating, which gave sufficient dispersion in the second order to isolate the lines which were to be resolved. The optical system was as shown in Fig. 4b, a cylindrical lens being used between slit and grating to correct the astigmatism of the grating so that horizontal interference patterns and vertical slit were focussed at the same time. This lens also magnified the size of the interference pattern by a factor of 8.

Proper exposures with combined Lummer-Gehrke plate and spectrograph proved to be ten or twenty times those necessary with the grating alone, so that the ^{plate III A}~~plate (blank)~~ of the $C'^2 - C'^2$ bands required about ten minutes exposure on an Eastman I J spectroscopic plate.

It may be seen from the staggering of successive members of the R_2 branch on this plate that although the Λ -type doublets should not perhaps be completely resolved because of the broadness of the interference patterns, their centers should be far enough apart to permit the desired intensity measurements. Failure to obtain the theoretical resolving power on this plate may be attributed to the width of the lines due to Doppler broadening, aberrations in the rather short-focus lens used to correct astigmatism, and to the fact that successive beams emerging from the plate were by no means of equal intensity for the angle of emergence used, $i \approx 80^\circ$. The expected Doppler broadening was calculated and should have been small for temperatures of the source under 2000°C . An angle $i \approx 80^\circ$ was used because the interference fringes were more intense than for larger i , and tests with the mercury line indicated that resolving power was not much impaired because of the unequal intensities of successive beams.

The source of the Swan bands was the water-cooled capillary discharge tube shown in Fig. 5. A few millimeters of methane was let into the tube and a discharge run which decomposed the methane and deposited carbon on the electrodes and in the capillary. The resulting hydrogen was pumped out and 11 mm. of argon let in. This argon pressure

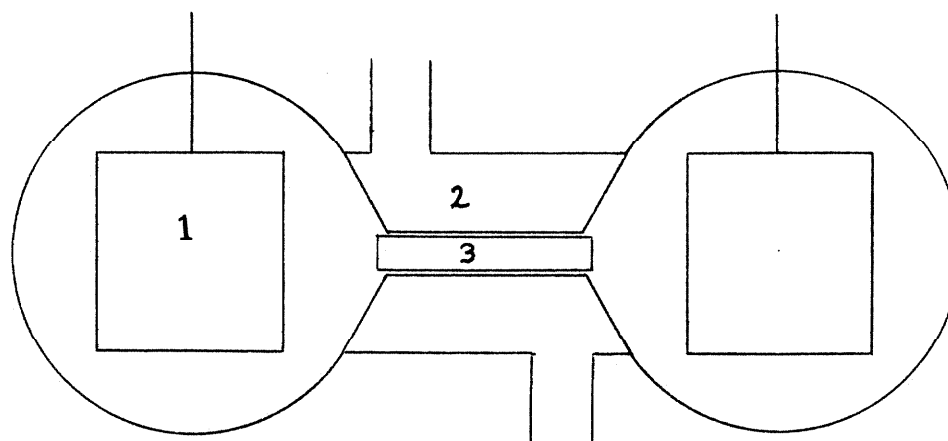


Fig. 5. The Discharge Tube

1. Hollow Cylindrical Electrode of Aluminum

2. Jacket for water-cooling

3. Porcelain capillary, I.D. 2 mm.

seemed to be rather critical. The tube was activated by a 1 K.W. transformer giving 20,000 volts, though the voltage across the tube was probably a small fraction of 20,000 volts due to poor regulation of the transformer. The porcelain lining in the capillary prevented the glass capillary from getting hot under these conditions and putting too much sodium vapour in the discharge.

Plate III B was the result of a 3-hr. exposure with enriched methane. About 75 c.c. of methane at 1 cm. pressure containing approximately 40% heavy methane was used. It may be seen that the $C^{12}-C^{13}$ lines are stronger than the $C^{12}-C^{12}$ lines and that the spectrum of $C^{13}-C^{13}$ shows up weakly. Unfortunately the interference pattern is not as sharp as in Plate III A, which is probably due to temperature changes of the ^{interferometer} plate during exposure, or to shifts in the optical system occurring during removal of the discharge tube for refilling with methane. Step weakener plates were sensitized and developed along with this plate so that intensity distributions for these patterns could be analyzed.

Results

The quickest way to determine the C^{13} spin, however, appeared to be a measurement of the staggering of the "center of gravity" of the combined components of the R_3 branch. The separation between the center of gravity of the R_3 and the R_2 lines was taken as the criterion of this staggering, and measurements of this separation made on about five fringes each of the lines 18, 19, and 20 of the $C^{12}-C^{12}$, $C^{12}-C^{13}$

and $C^{13} - C^{13}$ bands. The center of gravity of each pattern was judged by eye and measurements made on a comparator. The two Λ -type components of the $C^{12} - C^{13}$ band should be of equal intensity and consequently their center of gravity in normal position. The measured displacements of the three lines of these bands are as follows:

No.	$C^{12} - C^{12}$	$C^{13} - C^{13}$
18	+ .011 Å	-.015 Å
19	- .007	+.008
20	+ .015	-.015

From the consistency of data on each line, the errors in these values are very small, but systematic effects such as the influence of adjacent lines are probably the chief source of error. The separations are somewhat less than the value 0.018 predicted from previous measurements of the $C^{12} - C^{12}$ lines. The ratio of the displacement of $C^{13} - C^{13}$ to that of $C^{12} - C^{12}$ from these three lines is $1.17 \pm .08$.

From the theory presented above, the intensity of the doublet components are in the ratio $\frac{s}{s+1}$ or $\frac{s+1}{s}$ depending on the statistics obeyed by the nucleus. We can immediately conclude that the C^{13} nucleus obeys Fermi-Dirac statistics, since it shows a displacement in the opposite direction than does C^{12} which is known to obey Einstein-Bose statistics. The ratio of displacement of the centers of gravity of the $C^{13} - C^{13}$ and $C^{12} - C^{12}$ lines for various spins should be as follows:

Spin	Ratio
0	1
1/2	.5
1	.33
3/2	.25
2	.20
5/2	.17

From this, the spin of C^{13} would seem to be zero. But this would be very difficult to explain theoretically, for since the nucleus obeys Fermi-Dirac statistics, it must contain an odd number of elementary particles (see below) and have a half-integral spin. Additional evidence that the spin is not zero is given by that fact that the R_3 branch of $C^{13} - C^{13}$ appears appreciably less intense than the R_2 branch. The most reasonable explanation of a measured ratio of approximately 1 is that the spin is 1/2 and that the weak component, of intensity 1/3 that of the stronger, was too weak perhaps to produce much effect on the photographic plate or the eye's estimate of the center of gravity. Certainly a spin of 3/2, which would make the relative intensities of the doublet components 3:5, would be expected to influence the center of gravity of the combined lines appreciably.

Taking the R_2 branches of these bands as standards for the position of the R_3 branches may be questioned, since the triplet structure may vary from a line of $C^{12} - C^{12}$ to corresponding lines of $C^{12} - C^{13}$. The behavior of this triplet separation is difficult to

predict exactly, but the variation from band to band should be small, and any variation from the $C^{12}-C^{12}$ to the $C^{12}-C^{13}$ band should be very closely the same as from $C^{12}-C^{13}$ to $C^{13}-C^{13}$ and not influence the measured ratios. This may be part of the reason why the odd line 19 shows a different shift from the even lines, though the same ratio. There is some suggestion, too, of an anomaly in the Λ -type doubling of line 19 from previous measurements, though these are not accurate enough to make ~~this~~ ^{an anomaly} certain.

Microphotometer curves of the interference patterns of some of the $C^{13}-C^{13}$ lines showed marked asymmetry indicating the presence of the weak doublet component. A careful analysis of the shapes and centers of gravity of these curves should give more conclusive evidence on the spin of the C^{13} nucleus.

Comparison with Theory

The fundamental particles proton, electron, and neutron all have spins $1/2$ ¹⁾ and obey Fermi-Dirac statistics. If atomic nuclei are composed of these particles, some conclusions may be drawn concerning the statistics and spins of the nuclei.

Consider, for example, the wave functions for two identical nuclei each containing n of these particles. The wave function must be antisymmetric with respect to each of the particles, so if two

- 1) It is possible that the neutron has a spin $3/2$, but this does not affect the results of the present discussion.

similar particles in two different nuclei are interchanged, the wave function changes sign. If the nuclei are interchanged, this is equivalent to interchanging n particles, or changing the sign of the wave-function n times. Consequently nuclei should obey Fermi-Dirac or Einstein-Bose statistics according as they are composed of an odd or even number of fundamental particles.²⁾ The fact that the C^{13} nucleus obeys Fermi-Dirac statistics is, then, in conformity with the usual picture that it is composed of 6 protons and 7 neutrons.

The nuclear spin is a result of the spins of the particles of which it is composed and their orbital angular momenta. These momenta are supposed to obey the usual quantum-mechanical rules, so that orbital angular momentum exists only in integral multiples of \hbar and can add to the spins to give integral or half-integral total momentum to the nucleus according as the sum of the spins of the particles is integral or half-integral. Since the C^{13} nucleus obeys Fermi-Dirac statistics, it must be composed of an odd number of particles and have a half-integral spin.

To predict the exact way in which spins and orbital momenta add, it is necessary to use some kind of approximate model for the nucleus. Probably the Hartree and α -particle models have proved most useful in predicting qualitatively the characteristics of light nuclei. The Hartree model assumes a central field and so reduces the nuclear

2) This proof has been doubted, but a more rigorous proof is given by Ehrenfest and Oppenheimer, Phys. Rev., 37, 333 (1931).

problem to one very similar to the problem of electronic energy levels in an atom. The α -particle model has proved particularly successful for light nuclei which may be considered made up of an integral number of α -particles, or an integral number of α -particles plus or minus a neutron or proton. The most notable disagreement of the two models is in the predicted values for the spins of C^{13} and N^{13} . Calculations of Rose and Bethe¹⁾ using the Hartree model predict a spin of $1/2$ for the ground levels of these two nuclei while the work of Sachs²⁾ using the α -particle model predicts a spin of $3/2$. A spin of $1/2$ for C^{13} would, then, show that the assumptions underlying Sachs' calculation are incorrect, though it would not perhaps prevent the usefulness of the α -particle model in other cases.

1) Phys. Rev., 51, 205 (1937).

2) Phys. Rev., 55, 825 (1939).

Part III. Further Work with Heavy Carbon

It is regretted that the time required to obtain a high concentration of heavy carbon has left little time for measurements on this carbon. The following projects are made possible by the spectral plates and supply of enriched carbon on hand.

More Accurate Determination of the C^{13} Spin

Further measurements of the C^{13} - C^{13} interferometer patterns already obtained should be made. Perhaps it will prove necessary to take more plates of these or other lines to obtain conclusively the C^{13} spin.

Identification of Bands

A number of bands are known to be associated with the carbon bands, but have not been as yet satisfactorily analyzed or the carrier molecule positively identified. Isotopic carbon should make possible their identification. Some of the strongest of these bands have heads at 4770.0, 4836.2, 4911.9, 4996.8 Å. Johnson¹⁾ assigned vibrational numbers to these assuming the 4770 band represented the (0,0) transition since it was most intense. Fox and Herzberg²⁾ suggest the 4770 is the (10-9) transition of the Swan bands. It was noted that pictures of enriched carbon showed double heads on these bands due to the two isotopes. Since the 50% C^{13} shows only two heads of about equal intensity,

1) Royal Soc. Trans., 226, 185 (1926)

2) Phys. Rev., 52, 638 (1937)

it must be concluded that the carrier molecule contains only one atom of carbon. The directions and magnitudes of the isotopic shifts of the heads show that the (0,0) band of this system is covered up by the group of Swan bands at 4737, and so has escaped detection. The 4770 band is produced by a (0,1) transition. An exact measurement of the isotopic shifts should allow a fairly accurate determination of the mass of the rest of the emitting molecule, and perhaps the complete determination of this molecule.

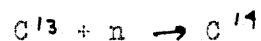
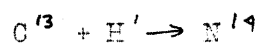
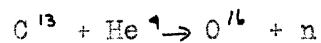
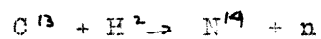
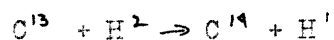
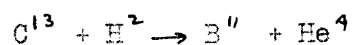
Mass Determinations

The ratio of masses of C^{12} and O^{16} has shown some discrepancy recently, so that a determination by band spectra methods should be worthwhile. A measurement of the shifts between the Swan bands of $C^{12}-C^{12}$, $C^{12}-C^{13}$, and $C^{13}-C^{13}$ will give the ratio of masses of C^{12} and C^{13} , while measurement of the shifts between the Ångström bands of $C^{12}-O^{16}$ and $C^{13}-O^{16}$ will determine the ratio of masses C^{12} and O^{16} in terms of the ratio C^{12} to C^{13} . The two combined measurements will give, then, the desired mass ratio C^{12} to O^{16} and in addition the ratio C^{12} to C^{13} . Both the Swan bands and Ångström bands show perturbations which should impede, but not prevent a fairly accurate determination of these quantities.

Nuclear Disintegrations

It was found that in running a discharge in methane a large part of the carbon from the disintegrating methane was deposited on

the electrodes. By running a discharge in enriched methane, therefore, a target of heavy carbon may be made for nuclear disintegration work. The reactions listed by Livingston and Bethe¹⁾ involving C^{13} which should give positive energies are the following:



The first three of these have been reported in ordinary carbon, but due to the small percentage of C^{13} in ordinary carbon their identifications are not certain nor the energies involved well known. The reaction $C^{13} + H^1 \rightarrow N^{14}$ is important because it has been suggested as part of a chain reaction which may be the source of stellar energies.²⁾ It is planned to attempt measurements on this reaction immediately.

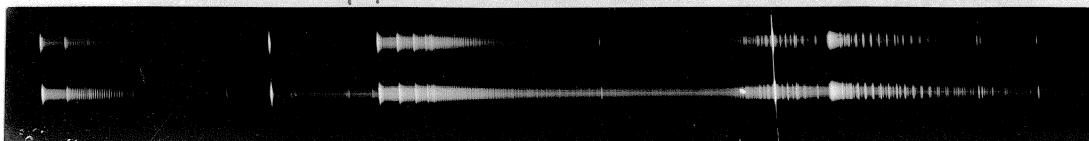
1) Rev. Mod. Phys., 9, 245 (1937)

2) Bethe, Phys. Rev., 54, 454 (1939)

Acknowledgement

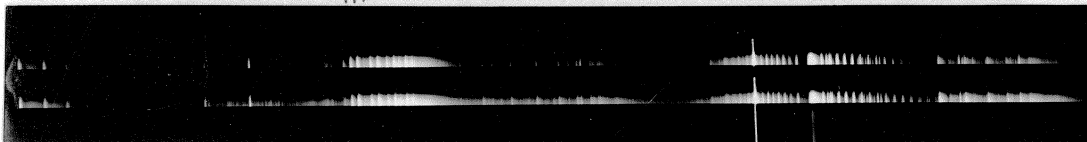
It is a pleasure to acknowledge the helpful direction and encouragement of Dr. Smythe throughout the course of this research, and the assistance of all those who have made available their knowledge and experience as well as the necessary apparatus and materials for this work - notably Drs. Bowen, Badger, and Sage, Mr. Clancy and Mr. Strong.

4 1



Ordinary Carbon, 0.7 Carbon Thirteen

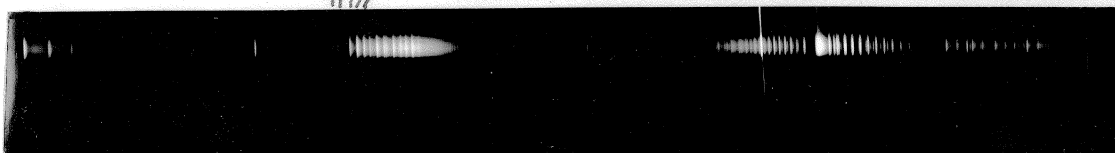
3 2 1



Enriched Carbon, 25-30% Carbon Thirteen

PLATE III

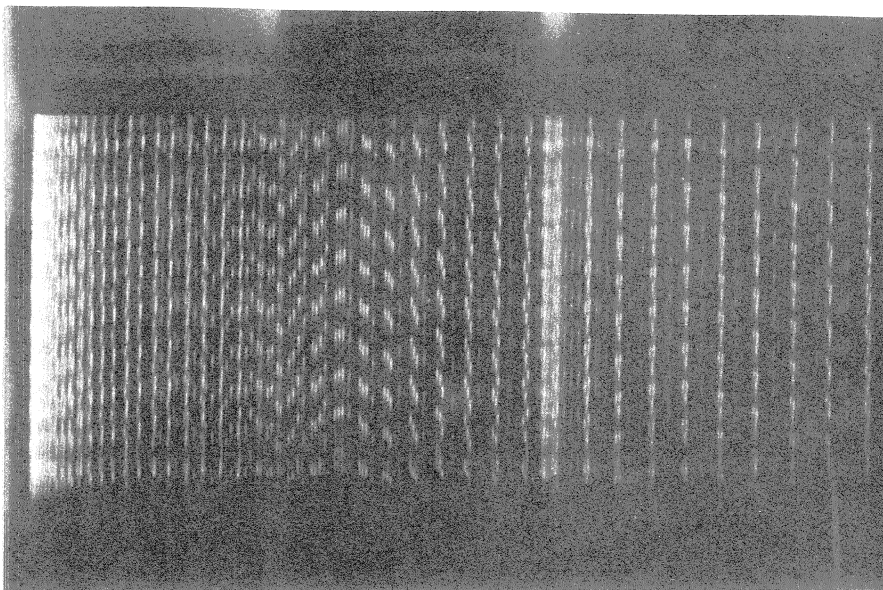
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Enriched Carbon, 45-50% Carbon Thirteen

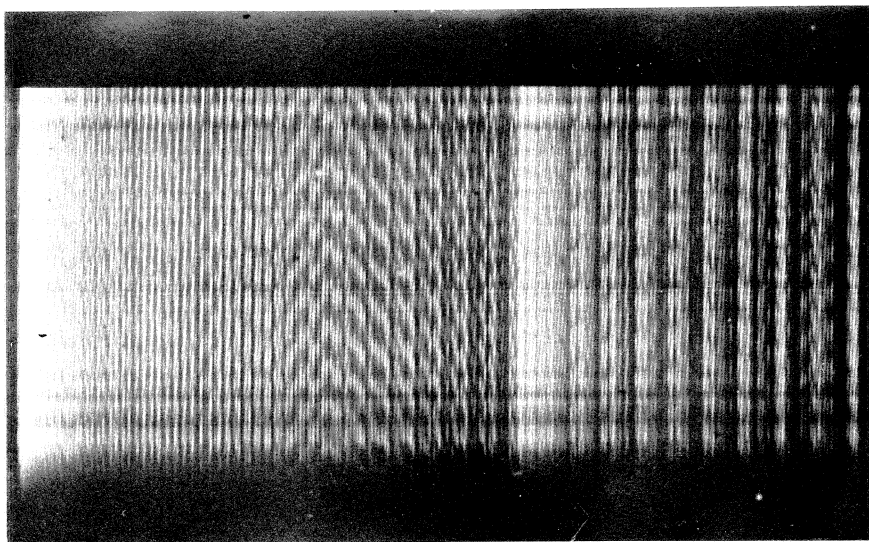
PLATE II

1. (1,0) band of Swan system due to $C^{12} - C^{12}$
2. (1,0) " " " " " " $C^{12} - C^{13}$
3. (1,0) " " " " " " $C^{13} - C^{13}$
4. Head of unidentified band
5. Isotopic head of unidentified band due to presence of carbon thirteen



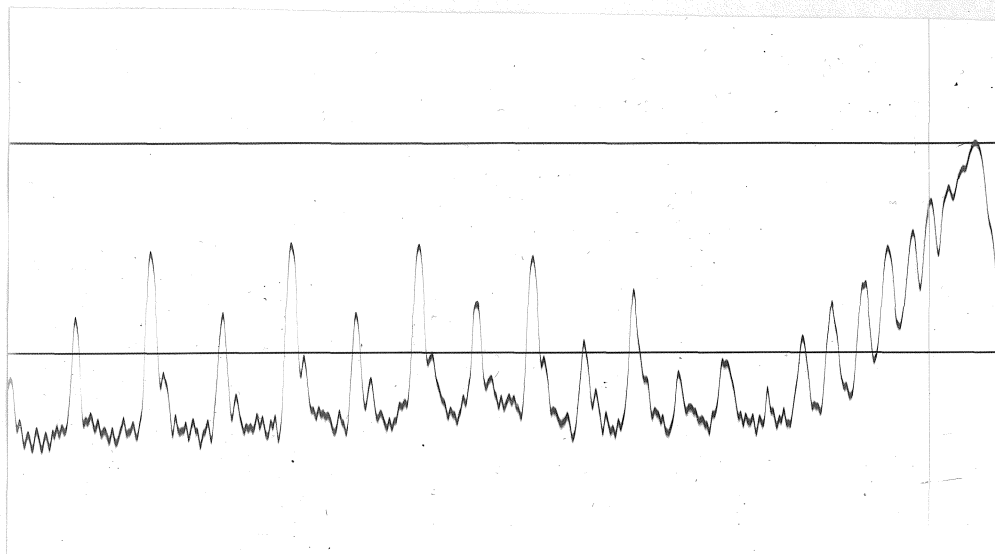
Two-fold enlargement of (6,0) Swan band taken
with Lummer Plate and 21-ft. grating. Ordinary carbon.

PLATE IIIA

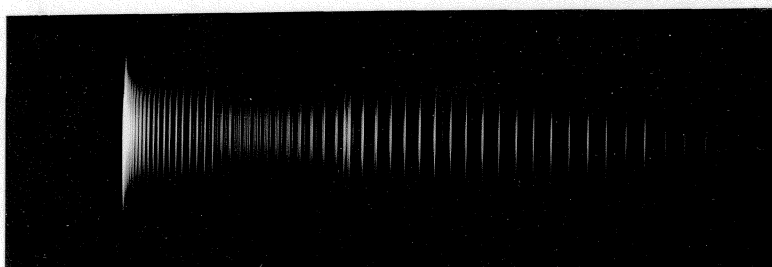


Same as above, but with 35-40% carbon thirteen

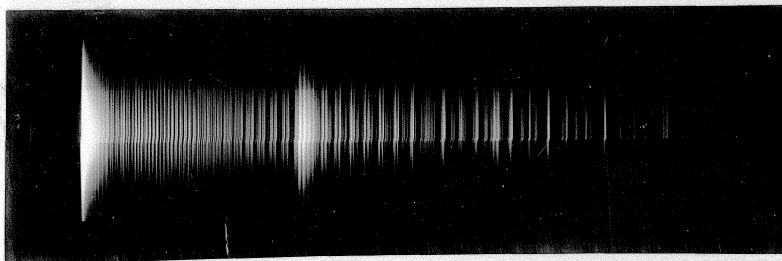
PLATE IIIB



Microphotometer curve showing alternating intensity of rotational lines of a negative band of N^4
Intensity ratio 1:2, spin 1.



(0,0) Swan band of ordinary carbon under high dispersion



(0,0) Swan band of carbon containing 30% C