

Determination of the Nuclear Spin of Cl^{37}

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The nuclear spin of the chlorine atom was determined by observing the line intensities in the band spectrum of the homonuclear diatomic molecule of that atom. The lines of even J values show a different intensity from those of odd J values, the ratio of intensities being given by $(I+1)/I$ where I is the nuclear spin of the atom in question. In the band absorption spectrum of chlorine the intensity ratio of lines of the $\text{Cl}^{35}\text{Cl}^{35}$ molecule has been measured and compared with the value found by Elliott. These values are in substantial agreement and yield a value of $5/2$ for the nuclear spin of Cl^{35} . In this spectrum no lines of the molecule $\text{Cl}^{37}\text{Cl}^{37}$ were observed due to the low con-

centration of Cl^{37} in the gas. By the method of thermal diffusion 200 cm^3 , S.T.P., of chlorine gas was obtained containing 45 percent Cl^{37} . The absorption spectrum of this gas showed lines of the $\text{Cl}^{37}\text{Cl}^{37}$ molecule in the $1 \rightarrow 12$ band of the ${}^1\Sigma \rightarrow {}^0$ band system of Cl_2 . For this band the alternating intensity ratio for the $\text{Cl}^{37}\text{Cl}^{37}$ molecule (1.28) was the same, within the experimental error, as for the $\text{Cl}^{35}\text{Cl}^{35}$ molecule (1.26), indicating that the nuclear spin of Cl^{37} is probably also $5/2$. In interpreting the intensity ratios one must take into account the overlapping of lines and general background present.

1. INTRODUCTION

IT is a well-known fact that homonuclear diatomic molecules and certain linear polyatomic molecules exhibit the phenomenon of alternating intensities in their band spectra. This intensity ratio arises from the fact that the statistical weights of rotational levels with (+) symmetry are different from the statistical weights of levels with (−) symmetry. This ratio can be shown to be

$$(I+1)/I$$

for homonuclear diatomic molecules where I is the nuclear spin of the nucleus of the element in the molecule. For polyatomic molecules the intensity ratio is more complicated. The nuclear spin of a nucleus may therefore be determined by observing and measuring the alternating intensity ratio in the band spectrum of its homonuclear diatomic molecule. Elliott¹ analyzed the ${}^1\Sigma \rightarrow {}^0$ band system of Cl_2 in absorption and made a determination of the alternating intensity ratio of the molecule $\text{Cl}^{35}\text{Cl}^{35}$. The value of this ratio was 1.35 from which he concluded that the most probable value of the nuclear spin of Cl^{35} is $5/2$. In several bands he was able to identify the lines of the molecule $\text{Cl}^{35}\text{Cl}^{37}$ but due to the small concentration of Cl^{37} (24.2 percent) he was not able to identify lines of the homonuclear mole-

cule $\text{Cl}^{37}\text{Cl}^{37}$. Elliott found no evidence of alternating intensities in the spectrum of $\text{Cl}^{35}\text{Cl}^{37}$. This agrees with theoretical predictions.

It is now possible, having obtained chlorine enriched in the heavy isotope, to obtain the band spectrum of $\text{Cl}^{37}\text{Cl}^{37}$ and make a determination of the nuclear spin of Cl^{37} .

2. EXPERIMENTAL

The spectrum of Cl_2 was obtained in absorption using a 21-foot concave reflection grating ruled 30,000 lines to the inch. An Eagle mounting was used which gave a dispersion of about 1.25 Å per millimeter in the first order.

Only a limited amount, approximately 200 cm^3 S.T.P., of "enriched" chlorine containing 45 percent Cl^{37} was available. For this reason an absorption tube was constructed to give the greatest absorption for this small volume of gas. The optical arrangement is shown in Fig. 1. The absorption tube was 2.5 meters long and 1.2 cm

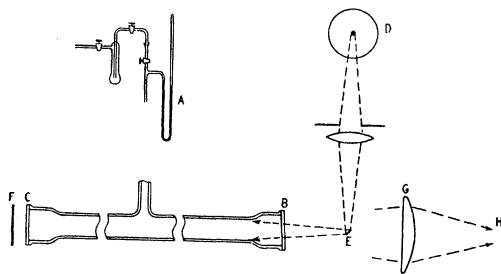


FIG. 1. Optical arrangement of apparatus.

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¹ A. Elliott, Proc. Roy. Soc. **123**, 629 (1929); **127**, 638 (1930).

inside diameter. After cleaning thoroughly with nitric acid and washing, windows were sealed on the previously ground ends of the tube. Chlorine was admitted to the evacuated tube. The pressure in the tube was measured by means of a mercury manometer protected by a thin layer of concentrated sulphuric acid. The tube was filled with Cl_2 to a pressure of 50 cm of mercury.

Light from a 100-candlepower Point-O-Lite lamp was focused on the small mirror *E* which reflected the light into the tube. A second aluminized mirror at the far end reflected the light back down the tube past mirror *E*, through cylindrical lens *G*, and onto the slit of the grating spectrograph. The plane glass window at the grating end of the tube was placed at a slight angle to prevent light from being directly reflected into the slit. This arrangement necessarily sacrifices light intensity in order to obtain sufficient absorption. An exposure time of 48 hours was required using a slit width of 0.03 mm.

The standard photometric technique using a step filter for plate calibration was employed. The step filter was calibrated by means of a photronic cell and a quartz monochromator. A Koch and Goos photographically recording microphotometer was used to reduce the spectrographic plate into an intensity curve. Each line was resolved graphically from its neighbors and its intensity calculated from plate calibration.

TABLE I. Wave-lengths, etc., of band lines in $\text{Cl}^{35}\text{Cl}^{35}$. Band 1→12. *P* and *R* branches.

J_P	J_R	λ in Å	ν in cm^{-1}	$\alpha(\text{max.})$
15	17	5164.77	19356.57	0.019
16	18	5165.86	19352.47	0.014
17	19	5167.03	19348.11	0.017
18	20	5168.26	19343.50	
19	21	5169.53	19338.74	0.016
20	22	5170.88	19333.69	0.019
21	23	5172.29	19328.42	0.020
22	24	5173.76	19322.93	0.013
23	25	5175.33	19317.06	0.015
24	26	5176.92	19311.13	0.013
25	27	5178.62	19304.80	0.014
26	28	5180.39	19298.22	0.013
27	29	5182.19	19291.49	0.014
28	30	5184.08	19284.46	
29	31	5186.03	19277.22	0.017
30	32	5188.04	19269.76	0.009
31	33	5190.14	19361.97	0.016
32	34	5192.21	19253.96	0.012
33	35	5194.51	19245.73	0.017

3. RESULTS AND DISCUSSION

a. Analysis of Spectrum of "Enriched" Chlorine

The strongest discrete absorption of chlorine is the band progression 1→11, 1→12, and 1→13, which lies between 5130Å and 5230Å. The electronic transition is $^1\Sigma \rightarrow ^+0$ and consequently each band consists of single *P* and *R* branches only.

TABLE II. Wave-lengths, etc., of band lines in $\text{Cl}^{36}\text{Cl}^{37}$. Band 1→12. *P* and *R* branches.

J_P	J_R	λ in Å	ν in cm^{-1}	$\alpha(\text{max.})$
11	13	5163.66	19360.72	0.020
12	14	5164.40	19357.97	0.020
13	15	5165.31	19354.55	0.020
14	16	5166.25	19351.03	0.024
15	17	5167.25	19347.29	0.026
16	18	5168.27	19343.47	
17	19	5169.40	19339.24	0.029
18	20	5170.58	19334.83	0.023
19	21	5171.86	19330.03	0.032
20	22	5173.14	19325.23	0.026
21	23	5174.53	19320.04	0.019
22	24	5175.94	19314.82	0.024
23	25	5177.44	19309.20	0.017
24	26	5179.02	19303.33	0.016
25	27	5180.64	19297.26	0.016
26	28	5182.38	19290.81	0.015
27	29	5184.09	19284.44	
28	30	5185.92	19277.62	
29	31	5187.78	19270.73	0.017
30	32	5189.77	19263.34	0.026
31	33	5191.79	19255.82	0.022
32	34	5193.88	19248.09	0.026

TABLE III. Wave-lengths, etc., of band lines in $\text{Cl}^{37}\text{Cl}^{37}$. Band 1→12. *P* and *R* branches.

J_P	J_R	λ in Å	ν in cm^{-1}	$\alpha(\text{max.})$
7	9	5163.85	19360.00	0.010
8	10	5164.25	19358.52	0.012
9	11	5164.91	19356.01	0.015
10	12	5165.57	19353.57	0.013
11	13	5166.41	19350.43	0.010
12	14			
13	15	5167.83	19345.12	0.013
14	16	5168.76	19341.25	0.011
15	17	5169.65	19338.39	0.016
16	18	5170.73	19334.26	0.009
17	19	5171.68	19330.71	0.0012
18	20	5172.79	19326.48	0.009
19	21	5174.12	19321.58	0.010
20	22	5175.33	19377.06	
21	23	5176.77	19311.68	0.013
22	24	5177.89	19307.44	0.008
23	25	5179.52	19301.46	0.010
24	26	5181.00	19296.00	0.005
25	27	5182.67	19289.73	0.008
26	28	5184.27	19283.75	0.005
27	29			
28	30	5187.58	19271.43	
29	31	5189.53	19264.20	0.007
30	32	5191.35	19357.47	0.008
31	33	5193.38	19249.93	0.010
32	34	5195.26	19242.98	0.008

In band 1→12 the P and R branches fall one on top of the other, the lines of one branch lying on the lines of the other whose J values are two removed. Hence even J values fall on even and odd on odd and the alternating intensity phenomenon is retained, not obliterated, as would be the case if even J value fell on odd J value.

From a spectrogram taken with the enriched chlorine it has been possible to identify 24 lines which belong to the molecule $\text{Cl}^{37}\text{Cl}^{37}$ in the

TABLE IV. Rotation constants of band 1→12 of $\text{Cl}^{37}\text{Cl}^{37}$.

B''	B'
0.1115 cm^{-1}	0.2228 cm^{-1}

1→12 band. Due to the increased complexity and over-lapping of lines it has been impossible to identify any lines in the 1→11 and 1→13 bands as belonging to the molecule $\text{Cl}^{37}\text{Cl}^{37}$.

Tables I, II, III give wave-lengths, etc., for the lines of the three molecules. The rotational constants are given in Table IV. The general appearance of the spectra of normal and enriched chlorine may be seen in Fig. 2.

The maximum value of the absorption coefficient, $\alpha(\text{max.})$, for a given line is calculated from the expression

$$I = I_0 e^{-\alpha \rho x},$$

where I is the intensity at the center of the absorption line, ρ is the chlorine concentration in gram molecules per liter, and x is the thickness of chlorine in cm. Elliott² studied the relations of slit widths and line shapes to the line intensities and found no appreciable error was introduced in neglecting their effect.

b. Alternating Intensity Measurements

Elliott's measurements on the alternating intensity ratio of $\text{Cl}^{35}\text{Cl}^{35}$ in band 1→12 of "normal" chlorine were repeated by the author. The value obtained was 1.31 as compared to Elliott's value of 1.34 for this band. The relative intensity of lines of the $\text{Cl}^{35}\text{Cl}^{35}$ molecule to lines of the $\text{Cl}^{35}\text{Cl}^{37}$ molecule was found to be 1.32 as against Elliott's value of 1.35 for the same ratio. These values are in agreement with each other within experimental error.

² A. Elliott, Proc. Roy. Soc. 127, 638 (1930).

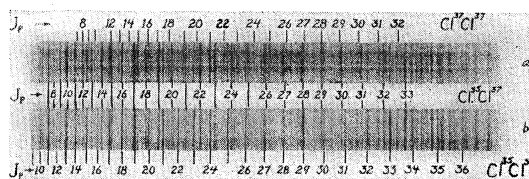


FIG. 2. Absorption spectrum of Cl_2 (band 1→12 of the $^1\Sigma \rightarrow ^0$ system). a is the spectrum of Cl_2 containing 45 percent Cl^{37} . b is the spectrum of Cl_2 containing 24.2 percent Cl^{37} . The rotational quantum numbers of the P branch are given for each molecule.

The alternating intensity ratios for the two homonuclear molecules were obtained from the spectrum of the "enriched" chlorine. These ratios were found to be 1.26 for $\text{Cl}^{35}\text{Cl}^{35}$ and 1.28 for $\text{Cl}^{37}\text{Cl}^{37}$. This ratio may be calculated in two ways. The first way consists of comparing the average intensity of all the strong lines to the average intensity of the weak lines. The second method consists of finding the intensity ratio of each line to its immediate neighbors and then averaging over all lines. These two methods give the same result in this particular case.

As was pointed out by Elliott the experimental values of the ratios should be regarded as lower limits since any background due to overlapping lines, etc., will make the measured ratio smaller than the true value. A background of less than 20 percent will raise Elliott's value 1.34 to 1.40 which is the theoretical value for a nuclear spin of $5/2$.

One would expect this background effect to be greater in the spectrum of the "enriched" chlorine since the intensity of all the lines is relatively less. This seems to be in accord with the measured values of 1.26 and 1.28 as the alternating intensity ratios in the spectrum of "enriched" chlorine. However since the intensity of the spectrum of $\text{Cl}^{37}\text{Cl}^{37}$ is comparable to the intensity of the spectrum of $\text{Cl}^{35}\text{Cl}^{35}$ the relative effect of the background may be neglected. It would appear then that the nuclear spin of Cl^{37} is the same as the nuclear spin of Cl^{35} . The most probable value of the nuclear spin of Cl^{35} is $5/2$ as determined by Elliott² and by the author from the spectrum of "normal" chlorine.

The author is indebted to Professor W. W. Watson, who suggested this problem, for his guidance and helpful suggestions.

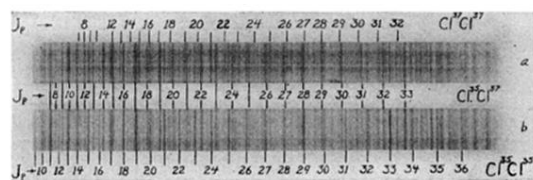


FIG. 2. Absorption spectrum of Cl_2 (band $1 \rightarrow 12$ of the $^1\Sigma \rightarrow ^4\Delta$ system). *a* is the spectrum of Cl_2 containing 45 percent Cl^{37} . *b* is the spectrum of Cl_2 containing 24.2 percent Cl^{37} . The rotational quantum numbers of the *P* branch are given for each molecule.