

THE ISOTOPE EFFECT IN BAND SPECTRA, IV: THE  
SPECTRUM OF SILICON NITRIDE

BY ROBERT S. MULLIKEN<sup>1</sup>

ABSTRACT

**Silicon nitride bands.**—(1) A system of bands shaded toward the red, lying between 3800 and 5300 Å was obtained by Jevons in 1913 by the introduction of SiCl<sub>4</sub> vapor into active nitrogen. His measurements have been repeated and extended to all possible heads. It is important that no oxygen be present. From a sharp intense head each band decreases rapidly in intensity to zero at the null line, then increases to a maximum at about  $m = 13$  in the negative branch, in which the lines get far enough apart to be resolved. With the aid of the quantum theory, Jevons' arrangement was revised, and correct initial ( $n'$ ) and final ( $n''$ ) vibrational quantum numbers assigned. The null lines of the Si<sup>28</sup>N bands correspond to the wave-number equation:  $\nu^{\circ} = 24234.2 + 1016.30 n' - 17.77 n'^2 + 0.410 n'^4 - 0.00487 n' - 1145.00 n'' + 6.570 n''^2$ . Partial analysis of the band structure indicates that the lines of any band are given by the equation:  $\nu = \nu^{\circ} + B' + 2B'm + Cm^2$  where  $B' = 0.728 - 0.097n'$  and  $C = -0.0121 - 0.0097n' + 0.0053n''$ ; from this the internuclear distance for the vibrationless SiN molecule is  $1.56 \times 10^{-8}$  cm. Additional weak heads are present whose positions agree very closely with those calculated for the isotopes Si<sup>29</sup>N and Si<sup>30</sup>N, isotope 29 being slightly the stronger. This agreement definitely excludes SiO or any other compound than SiN as the emitter of the bands, confirming the chemical evidence. The agreement is also definite, but not conclusive, evidence against the existence of half-quantum numbers for SiN, a result opposite to that for BO. Plate I shows most of the Si<sup>28</sup>N bands together with some isotope heads. The intensity distribution in each band corresponds to thermal equilibrium at about 80°C. In respect to the initial vibrational quantum number, the distribution is non-thermal and corresponds to a high effective temperature as in other cases such as BO and CN. The intensity distribution with respect to  $\Delta n$  is similar to that of the violet CN bands. The sequence  $\Delta n = 0$  is by far the strongest, other sequences of diminishing intensity being observed as far as  $-3$  and  $+3$  or  $+4$ . (2) *New system of bands*, extensive but weak, probably also due to SiN, is described. They all have double heads ( $\Delta\nu = 27$ ), are shaded toward the red and extend from the ultraviolet through the green. An equation for the heads is given. The intensity distribution is characterized by numerically large values of  $\Delta n$  and by the absence of the band ( $0 \rightarrow 0$ ) and some neighboring bands.

INTRODUCTION

IN 1913 Jevons described<sup>2</sup> an interesting band spectrum obtained by the introduction of silicon tetrachloride vapor into active nitrogen, and consisting in a system of bands, shaded toward the red, lying in

<sup>1</sup> National Research Fellow.

<sup>2</sup> W. Jevons, Roy. Soc. Proc. **89A**, 187 (1913-14).

the region between  $\lambda 3800$  and about  $\lambda 5300$ . Jevons ascribed the bands to a nitride of silicon, this being supported by the fact that they were not obtained by the discharge through pure  $\text{SiCl}_4$  and by the further fact that a nitrogen-containing product was deposited on the walls of the nitrogen afterglow tube during the emission of the bands. As Jevons pointed out, the action of active nitrogen on  $\text{SiCl}_4$  is similar to its action on carbon compounds, the cyanogen bands being emitted in the latter case. Many of the bands, according to Jevons, show a minimum of intensity about  $4A$  from the head, a similar phenomenon being observed in the cyanogen bands when produced in active nitrogen. Jevons arranged all the bands in rows and columns such that the successive intervals of frequency taken vertically and horizontally form arithmetical progressions (the intervals being substantially constant in a given row or column of frequency-intervals), and from these he determined the constants of a Deslandres equation.

In addition to the data on the heads of the silicon nitride bands, Jevons gives a list of silicon lines which are emitted at the same time. In the present work, one additional Si line was found, that at  $\lambda 4103.1$ , and possible indications of one or two others.

In the light of the quantum theory of band spectra, it is now evident that the intensity minimum observed by Jevons in many of the bands must represent the region of the null-line, or missing line, which is of much more importance from a theoretical standpoint than the usually much more obvious head. The unusual prominence of the null-line here must be ascribed to the low temperature of active nitrogen; this subject has been discussed by Birge in the analogous case of the cyanogen bands.<sup>3</sup> The null-lines are plainly visible in two of the bands in Jevons' reproductions, and are particularly well brought out in photographs taken by the present writer (cf Plate I). The structure of the bands is of a simple type (probably like that of the violet cyanogen bands) which in the light of the quantum theory, shows that they are due to a diatomic emitter. That they are due to the compound  $\text{SiN}$  is probable from the chemical evidence (including that above cited and new evidence given below), and is definitely proved by the isotope effect (see below).

A re-examination of the silicon nitride spectrum was undertaken by the writer in 1923 with the object of studying the expected isotope effect. At this time Si was known from Aston's positive ray work<sup>4</sup>

<sup>3</sup> R. T. Birge, *Astrophys. J.* **55**, 273 (1922).

<sup>4</sup> F. W. Aston, *Isotopes*, 2nd ed. p. 77 (1924).

to contain a small amount of an isotope 29 in addition to the dominant isotope 28; there was also doubtful evidence of an isotope 30 in small amounts, the doubt being occasioned by the possible presence of H compounds of the same mass-number. Jevons' data on the SiN bands evidently refer to Si<sup>28</sup>N heads, and include no measurements which can be attributed to Si<sup>29</sup>N or Si<sup>30</sup>N heads. New photographs by the writer showed clearly, however, that each favorably located Si<sup>28</sup>N head of sufficient intensity is accompanied by two approximately equally spaced weak satellites at the theoretically expected positions for Si<sup>29</sup>N and Si<sup>30</sup>N, isotope 29 appearing to be slightly more abundant than isotope 30. This was reported in a letter to *Nature*.<sup>5</sup> The existence of isotope 30 was later confirmed by Aston by the positive ray method,<sup>6</sup> it being found slightly less abundant than 29, in agreement with the results on the SiN bands.

In order to determine the theoretical positions of the isotope heads, vibrational quantum numbers were assigned to the bands measured by Jevons, making use of the latter's arrangement of the bands in rows and columns, and merely changing his empirical numbers  $m = 22, 21, \dots, 12$  and  $p = 55, 54, \dots, 50$ , to  $n' = 0, 1, \dots, 10$  and  $n'' = 0, 1, \dots, 5$ ,  $n'$  being the vibrational quantum number of the initial electronic state of the molecule,  $n''$  that of the final state. Measurements were also made on the null-lines, using Jevons' measurements on the heads as reference standards, and an equation for the null-lines in terms of  $n'$  and  $n''$  was obtained.<sup>7</sup> On this basis, the isotope effect showed good agreement with theory for the final state of the molecule but was abnormally large for the initial state, especially for large values of  $n'$ ; this anomaly was associated with various other peculiarities for the initial state, in particular with an extraordinary low vibration frequency as compared with that of the final state.<sup>5,7</sup> Complete new measurements of the heads and null-lines of the SiN bands were recently made, in order to be more certain as to the reality of the abnormal isotope effect, and in order if possible to find a means of avoiding it. With the new data, which differ considerably from those of Jevons in a few cases, the above arrangement of the bands in rows and columns now gives rather small, but definite and systematic, deviations from the constancy required by the combination principle for the frequency-intervals between neighboring rows, or neighboring

<sup>5</sup> R. S. Mulliken, *Nature*, March 22, 1924.

<sup>6</sup> F. W. Aston, *Nature*, Aug. 23, 1924.

<sup>7</sup> Paper presented before Am. Phys. Soc.; abstract in *Phys. Rev.* **23**, 554 (1924).

columns. By an arrangement of the bands differing radically from the old, it is found possible to satisfy completely the requirements of the combination principle and thus be sure that the new assignment of vibrational quantum numbers is correct. With this assignment, all the previous peculiarities and anomalies disappear and the isotope effect, in particular, is found to be in complete agreement with the theory. The former plausible but incorrect assignment is now seen to have been due to an unusual combination of misleading circumstances and relations. For the *heads*, it may be noted, the constancy of the frequency intervals is better with the old assignment; but this is of course of no theoretical importance.

#### EXPERIMENTAL PROCEDURE IN PRODUCTION AND MEASUREMENT OF BANDS

*Production of bands; evidence on nature of emitter.* The bands were obtained by the same general method as that of Jevons, using active nitrogen. In the latter part of the work, the same apparatus was used as in the work on the copper halide bands,<sup>8</sup> except that the bulb containing the silicon chloride, instead of being heated as in the case of the copper salts, was separated from the afterglow tube by a stopcock to control the flow of SiCl<sub>4</sub> vapor, SiCl<sub>4</sub> being a very volatile liquid. The SiCl<sub>4</sub> used was some material, free from CCl<sub>4</sub> in particular, which had been especially purified in connection with atomic weight work and which was kindly made available by Professor G. P. Baxter.

As noted in a previous paper,<sup>9</sup> the purple glow of the SiN bands is obtained in good intensity only when the nitrogen used is very free from oxygen, this behavior being in marked contrast to that of the BO bands and constituting strong evidence for the nitride origin of the present bands. Photographs were taken of an arc between silicon electrodes in an atmosphere of nitrogen in the hope of finding the SiN bands and getting additional evidence as to their nitride origin; but they were not present, perhaps because of a trace of oxygen impurity. The silicon arc in air gives oxide bands.<sup>10</sup> Apparently at high tem-

<sup>8</sup> R. S. Mulliken, *Phys. Rev.* **26**, p. 1 (July, 1925); cf. Fig. 1 and p. 7-8.

<sup>9</sup> R. S. Mulliken, *Phys. Rev.* **25**, 259-94 (1925). See p. 277.

<sup>10</sup> A. del Campo, *An. Soc. Esp. de Fis. Quim.* **13**, 98 (1913); A. del Campo and J. Estalella, *ibid* **20**, 586 (1922); C. Porlezza, *Atti. accad. Lincei* **31** (ii) 513 (1922), and *Gazz. Chim. Ital.* **53**, 215 (1923); W. Jevons, *Roy. Soc. Proc.* **106A**, 174 (1924). The bands, which are those of a diatomic emitter, are in all probability due to SiO, since the presence of oxygen is required (del Campo, Jevons). The heads can be represented by the equation (cf R. Mecke, *Phys. Zeit.* **26**, 239, 1925)  $\nu = 42,643 + 844.5 n' - 5.8 n'^2 - 1236.0 n'' + 6.04 n''^2$ .

peratures the affinity of silicon for oxygen exceeds that for nitrogen, while the fact that the carbon arc in air gives the CN bands indicates that the reverse is true for carbon.

*New photographs and measurements.* The photographs were obtained with the Hilger glass prism spectrograph used in previous work on BO and CuI, and all precautions were taken to secure the best possible definition. Greatly enlarged reproductions from one of the photographs are shown in Plate I. For the measurements, three photographs were used with a copper arc and three others with an iron arc comparison spectrum. Detailed measurements were made on one of these, and enough measurements on the others to make sure that they all gave consistent results, showing the absence of appreciable displacements in the comparison spectra. As in the case of the BO bands,<sup>11</sup> the results differed appreciably from those of Jevons, being consistently lower by 2–3 wave-number units in the region from  $\lambda 3950$  to  $\lambda 4360$ , but differing irregularly in the region of longer wave-lengths, being for the most part a few or even several units higher. For the weaker bands, these differences may be ascribed to inaccuracy in Jevons' measurements, in accordance with his statement that the accuracy is low for these bands. The consistently lower present results in the short-wave-length region of stronger bands are more difficult to explain. In the case of BO, it was suggested that such a difference might arise if in Jevons' measurements the setting was made on the extreme high-frequency edge of the head, while in those of the writer it was made at the point of maximum blackening, the heads being treated like lines. A comparison of the two methods of setting for a number of the SiN bands gave an average difference for the two methods of about 0.010 mm, the difference being surprisingly constant for bands of greatly varying intensity and structure. Since this difference corresponds to an average of only about 1.1 wave-units with the dispersion used, the suggested explanation is evidently inadequate to account for the discrepancy between the present results and those of Jevons. No further attempts have been made to determine the cause of the discrepancy, since a possible small constant error is obviously of minor importance in the theoretical interpretation of the data. The data on heads given in the following tables were all obtained by the method of setting on the point of maximum blackening for each head.

Measurements were made on the heads of all possible Si<sup>28</sup>N bands. The ultraviolet was photographed with a quartz spectrograph, in order

<sup>11</sup> Mulliken, loc. cit<sup>9</sup>, p. 267-8.

## DESCRIPTION OF PLATE I.

Beginning with the top row, the reproductions show the entire SiN spectrum between  $\lambda 3986$  and  $\lambda 4800$ . They were made in four sections from a single negative; each junction point is indicated by a dot *above*; in each successive section a somewhat more heavily exposed print was used than for its neighbor to the left in order to show both strong and weak heads to best advantage. Except for this (and an undue weakening of the bands at the high-frequency end due to prism absorption, and of the 7,9 band at the other end by decreasing plate sensitivity) the reproduction gives an essentially correct idea of the intensity distribution.

The *head* of each *A* band of Si<sup>28</sup>N is marked with a line, and the vibrational quantum numbers ( $n'$ ,  $n''$ ) are given. In the case of the more intense bands, the fall of intensity from the head to the null-line, and the rise to a maximum in the negative branch before the final fading out, are well shown. The weak Si<sup>29</sup>N and Si<sup>30</sup>N heads, which are at the left of the corresponding Si<sup>28</sup>N heads, are marked when visible. The pairs of dots under the lowest section of the plate indicate the positions of the heads of some of the *new* bands; beginning at the left, the (1,5), (0,5), (1,6), and (2,7) head-pairs are marked; of these (1,5) is the most clearly visible. Unmarked conspicuous heads or lines (aside from structure lines of the bands) are of unknown origin (cf Table VI).

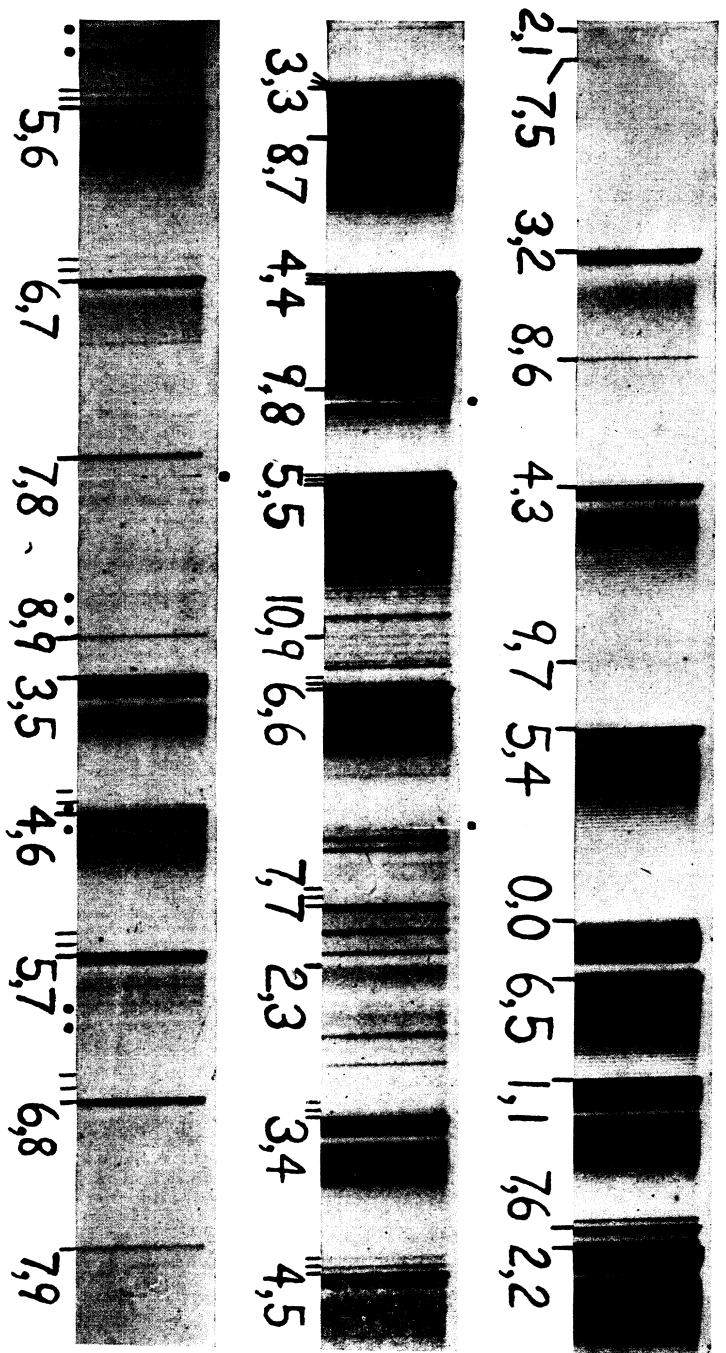


PLATE I. The entire band spectrum of SiN from 2175 (top) to 79 (bottom).

to measure a few heads which were not transmitted by the glass prism. Some new bands of a different type were also found; other new bands were also found in the green (see later section).

The *null-lines* of as many SiN bands as possible were measured on the plates, the setting being made at the point of minimum intensity. In some bands where the head is at a considerable distance from the null-line, the latter appears as a distinct narrow gap in the shading; in others where it is nearer, as a mere lightening; these effects can be seen in the reproductions (Plate I). Settings on the null-lines are subject to rather greater uncertainty than in the case of heads, but it is thought that the data are nearly as accurate as for the latter. One cause of error is the asymmetry in the rate of increase of blackening on the two sides of the null-line. This should tend to displace the settings away from the heads, but study of the question indicates that the error so introduced is unimportant. In the case of bands where the null-lines were not directly measurable, their positions were calculated from those of the corresponding heads, the necessary correction being obtained from a study of the manner in which the distance from head to null-line varies with the vibrational quantum numbers in the directly measurable cases (see next section).

Measurements on the Si<sup>29</sup>N and Si<sup>30</sup>N heads, made wherever possible, are given in Table II. Measurements on null-lines were here impossible, since these are concealed by the shading of the much more intense Si<sup>28</sup>N bands.

#### RESULTS OF MEASUREMENTS ON SiN BANDS

*Analysis of band structure.* The bands consist of two branches, one starting in each direction from the null-line, the positive branch (starting toward higher frequencies) forming a head. The bands are not resolved near the null-line, nor anywhere in the positive branch; but in the negative branch, they become resolved at a moderate distance from the null-line, and can be followed for some distance (cf Plate I). It is reasonable to assume, in accord with their general appearance, that the bands are of the same type as the violet cyanogen bands, with a single missing line (the null-line) in the otherwise continuous series of lines expressible by the equation<sup>12</sup>

$$\nu = \nu^{\circ} + B' \pm 2B'm + Cm^2. \quad (1)$$

In Eq. (1) the positive and negative signs refer to the positive and negative branches, respectively;  $m$ , denoting the rotational quantum

<sup>12</sup> Cf A. Sommerfeld, *Atombau und Spektrallinien*, 4th ed., pp. 718-34.



number of the final state, is assumed to have half-integral values; for the null-line,  $m = -1/2$ ;  $\nu^\circ$  corresponds to the change of electronic plus vibrational energy.

Measurements were made on the resolved negative branch lines of the (3,2), (4,3), (5,4), and (4,4) bands, which are at the violet end of the spectrum, where resolution is most complete. By plotting first differences of successive lines, the coefficient  $C$  was determined for each of these bands; these values of  $C$  are given in Table I. Substitution of  $m = -1/2$  in Eq. (1) gives for the null-line  $\nu = \nu^\circ + \frac{1}{4}C$ , which is equal within experimental error to  $\nu^\circ$ , the wave-number of the band-origin,<sup>13</sup> since  $\frac{1}{4}C$  is here negligible. For the head,<sup>12</sup>  $\nu = \nu^\circ + B' - B'^2/C$ . Letting  $H$  represent the distance from null-line to head, we then have,

$$H = B' - B'^2/C. \quad (2)$$

The  $H$  values are obtainable from the data of Table II, and it is now possible to obtain  $B'$  for each of the four bands; the results are given in Table I.<sup>14</sup>

TABLE I

*Experimental values of  $B'$  and  $C$ .*

[Note: The data in bold-face type were determined from measurements on structure lines; the remaining data were calculated from the  $H$  data of Table II ( $H$ =distance from null-line to head) assuming  $B'$  values calculated from Eq. (3). The data are all in wave-number units.]

$n'$	$n''$	$B'$	$-C$	$n'$	$n''$	$B'$	$-C$	$n'$	$n''$	$-C$
3	2	<b>0.686</b>	<b>0.0303</b>	3	3		0.0245	4	5	0.0255
4	3	<b>0.685</b>	<b>0.0365</b>	4	4	<b>0.704</b>	<b>0.0305</b>	5	6	0.0288
5	4	<b>0.680</b>	<b>0.0403</b>	5	5		0.0336	6	7	0.0323
0	0		0.0117	6	6		0.0384	3	5	0.0152
1	1		0.0161	7	7		0.0441	4	6	0.0198
2	2		0.0199	2	3		0.0161	5	7	0.0244
				3	4		0.0210	6	8	0.0264

Now  $B'$  should be expressible in the form  $B' = (h/8\pi^2 J') - a'n' = B_0' - a'n'$ , and  $C (=B' - B'')$  in the form  $C = C_0 - a'n' + a''n''$ . From the data on  $C$  for the four measured heads, preliminary values of  $a'$ ,  $a''$ , and  $C_0$  can be obtained. From  $a'$  and the  $B'$  data for the four bands, a preliminary value of  $B_0'$  is then obtained, and from it and  $a'$  can be calculated the  $B'$  value for each value of  $n'$ . From these and the  $H$

<sup>13</sup> Cf R. S. Mulliken, Phys. Rev. 25, 119-138 (1925). For definition of "origin," see p. 123.

<sup>14</sup>  $B'$  could also be obtained by extrapolating the first difference curve (a straight line) in a suitable way to the null-line, but this method is incapable of accuracy. The values of  $B'$  and  $C$  given in Table I were, however, obtained by adjusting the curve in such a way as to give a correct extrapolation to the null-line and at the same time to agree with the measured values of  $H$ .

values obtainable from the data of Table II, a large number of  $C$  values (see Table I), corresponding to a variety of combinations of  $n'$  and  $n''$ , can be calculated; and from these, more accurate values of  $\alpha'$ ,  $\alpha''$ , and  $C_0$  than before can be obtained. By repeating the calculation of  $B_0'$  with the new value of  $\alpha'$ , and so on, by successive approximations (one or two suffice), the following results are obtained:

$$B' = 0.728 - 0.0097 n'; C = -0.0121 - 0.0097 n' + 0.0053 n''. \quad (3)$$

From Eq. (3) the values of  $B'$  and  $C$ , and so of  $H$ , can be calculated for *any* values of  $n'$  and  $n''$ . Values of  $H$  so obtained were used to reduce the data of Table II, in the cases where heads alone could be measured, to the corresponding values for null-lines. It should be noted that calculated values of  $H$  for this purpose could have been obtained in a purely empirical way from the measured values by studying the way in which the latter vary with  $n'$  and  $n''$ . The results would have been only slightly different, so that the subsequent analysis of the null-line data is practically independent of any possible doubts as to that of the band structure. The procedure actually used amounts to employing the theory as a means of determining the functional relation of  $H$  to  $n'$  and  $n''$ , and then using the measured values of  $H$  to determine the necessary constants so as to calculate unmeasured  $H$  values.

*Dimensions of SiN molecule.* From the above-determined values of  $B_0'$  and  $C_0$ , can be calculated the moment of inertia and interatomic distance of the vibrationless SiN molecule in its initial and final electronic states. From  $B_0'$  one gets  $J_0' = 3.78 \times 10^{-39}$  gm cm<sup>2</sup>, and  $r_0' = 1.567 \times 10^{-8}$  cm. From  $B_0'' (= B_0' - C_0)$  one gets  $J_0'' = 3.72 \times 10^{-39}$  gm cm<sup>2</sup>, and  $r_0'' = 1.554 \times 10^{-8}$  cm. The values of  $r_0$  are considerably greater, as would be expected, than for the CN molecule, where  $r_0$  is  $1.17 \times 10^{-8}$  cm for what is probably the normal state.

Although the writer believes that the foregoing analysis is correct, it would obviously be desirable to study the bands under sufficient dispersion to give complete resolution in the region of the null-lines at least. Also, it may well be that the band lines, which appeared single with the dispersion used, actually consist of narrow doublets as in the violet CN bands.

*Analysis of null-line data.* In order to obtain an equation for the null-lines of the SiN bands, it is convenient to arrange the null-line data of Table II in a rectangular array like Table III, merely substituting them for the intensities of Table III. By an analysis of data

TABLE II  
Wave-number data on  $S_1N$  bands<sup>1</sup>

Vibr. num. $n' n''$	Si <sup>28</sup> N bands				Isotopic displacements <sup>5</sup>					
	Head	J-M <sup>2</sup>	Null-line <sup>3</sup> O-C <sup>4</sup>		Si <sup>29</sup> N heads			Si <sup>30</sup> N heads		
					Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>	Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>
6 3	26402		26393	-5						
7 4	26135		26127	-4						
8 5	25863		25856	0						
9 6	25577		25571	-4						
2 0	26213	-1	26196	-3						
3 1	26007		25993	-2						
4 2	25787		25775	-1						
5 3	25554	3	25543	-1						
6 4	25309.7	3	25299.9	0						
7 5	25054.7	3	25045.9	0						
8 6	24790.8	3	24782.9	-1						
9 7	24518		24511	-5						
1 0	25259.1	2	25234.8	2						
2 1	25080.3	2	25060.5	0						
3 2	24886.5	3	<b>24870.3</b>	0						
4 3	24678.4	3	<b>24664.8</b>	1						
5 4	24457.0	2	<b>24444.8</b>	0						
6 5	24223.9	3	24213.0	-1						
7 6	23981.8	3	23972.1	-1						
8 7	23731.4	4	23722.7	-1						
9 8	23473	-7	23465	-3						
10 9	23212		23205	-4						
0 0	24280.6	3	<b>24234.5</b>	0	-0.5	-0.5	.....	-1.0	-1.0	.....
1 1	24127.8	2	<b>24095.0</b>	0	-0.4	+0.5	.....	-0.7	+1.0	.....
2 2	23960.4	2	<b>23934.5</b>	-1	-0.2	1.7	.....	-0.5	3.2	.....
3 3	23778.3	2	<b>23757.7</b>	0	-0.2	3.0	3.1	-0.4	5.7	5.5
4 4	23581.7	2	<b>23564.6</b>	0	-0.2	4.4	4.5	-0.3	8.4	8.8
5 5	23372.9	2	<b>23358.5</b>	0	-0.1	6.0	5.4	-0.2	11.2	11.2
6 6	23152.9	2	<b>23140.6</b>	0	-0.1	7.6	6.9	-0.1	14.3	15.1?
7 7	22924.1	3	<b>22913.6</b>	0	-0.1	9.2	10.0	-0.1	17.3	18.7
8 8	Masked by or fused with 3,4 head									

Si<sup>29</sup>N and Si<sup>30</sup>N heads concealed in this region by shading of Si<sup>28</sup>N heads.

<sup>1</sup> For intensity data, see Table III. For the isotope heads, the intensities are all very low (0 to 000), as can be seen from Plate I.

<sup>2</sup> J-M = excess of Jevons' measured wave-number over the writer's. Blanks in this column represent bands not measured by Jevons.

<sup>3</sup> The values in bold-face type were measured directly. The other values were calculated from the data on the heads with the help of Eqs. (2) and (3): see discussion in paragraph following Eq. (3).

<sup>4</sup> O-C = Observed minus calculated. The calculated values are from Eq. (4).

<sup>5</sup> Isotopic displacement = wave-number of Si<sup>29</sup>N or Si<sup>30</sup>N head minus that of corresponding Si<sup>28</sup>N head.

<sup>6</sup> The calculated isotopic displacement for any head consists of two parts, a small (negative) *rotational* contribution (for method of calculation see second paragraph under "Confirmation of the isotope effect") and a larger *vibrational* contribution (see third paragraph under "Confirmation of isotope effect"). The "calc." (calculated) displacement is the sum of these two contributions, of which only the former is given explicitly in the table.

<sup>7</sup> The deficiency of observed data in the low-frequency part of the spectrum is in all cases attributable to insufficient intensity of the isotope heads, or, when so stated in the table, to masking by structure lines from a preceding head.

TABLE II—continued  
 Wave-number data on SiN bands<sup>1</sup>

Vibr. num. <i>n'</i> <i>n''</i>	Si <sup>28</sup> N bands				Isotopic displacements <sup>2</sup>					
	Head	J - M	Null-line	O - C <sup>4</sup>	Si <sup>29</sup> N bands			Si <sup>30</sup> N heads		
					Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>	Rotl. <sup>6</sup>	Calc. <sup>6</sup>	Obs. <sup>7</sup>
0 1	Not found									
1 2	Not found (although reported by Jevons)									
2 3	22856.6		<b>22824.6</b>	2	Masked by structure lines, etc., but also apparently abnormally weak.					
3 4	22684.5	-4	<b>22660.6</b>	2						
4 5	22499.8	0	<b>22480.5</b>	1	-0.2	10.3	9.5	-0.4	19.8	19.6
5 6	22302.4	2	<b>22285.7</b>	0	-0.1	11.7	11.2	-0.2	22.4	22.3
6 7	22094.6	2	<b>22080.1</b>	-1	-0.1	13.2	13.4	-0.2	25.1	25.7
7 8	21878.5	-2	21866.3	0	-0.1	14.7	15.5	-0.2	27.8	31.2?
8 9	21656.2	-8	21645.5	1	Masked by structure lines, etc.					
0 2	Not found									
1 3	Not found									
2 4	21772.3		21723.3	-1						
3 5	21605.6	-10	<b>21572.8</b>	0						
4 6	21431.6	-2	<b>21407.0</b>	1	-0.2	16.0	15.2	-0.4	30.9	31.6
5 7	21246.3	-2	<b>21226.8</b>	0	Present but masked by structure lines.					
6 8	21052.0	-5	<b>21035.3</b>	0	-0.1	18.6	19.1?	-0.2	35.7	37.2?
7 9	20848.8	-9	20834.7	1						
8 10	20637.5		20625.4	1						
9 11	20415		20404	-4						
4 7	20381.2		20346.5	0						
5 8	20206.0	2	20180.2	0						
6 9	20021.3		20000.9	-1						
7 10	19830.4		19813.7	0						
8 11	19631		19617	0						
9 12	19421		19409	-5						
6 10	19006		18980	-1						

TABLE III

*Intensity distribution in Si<sup>28</sup>N bands*, The intensities are estimated photographic intensities for a green-sensitive plate, and apply to each band as a whole, not to its head; for data on the heads, reference may be made to Jevons' paper.<sup>2</sup> The  $\Delta n=0$  sequence is indicated by the use of bold-faced type.

<i>n''</i> →	0	1	2	3	4	5	6	7	8	9	10	11	12
<i>n'</i> 0	<b>5</b>	...	...	...	...	...	...	...	...	...	...	...	...
↓ 1	0	<b>4</b>	...	...	...	...	...	...	...	...	...	...	...
2	000	1	<b>6</b>	1	2	...	...	...	...	...	...	...	...
3	...	0-	2-	<b>10</b>	3	3	...	...	...	...	...	...	...
4	...	...	0	2	<b>8</b>	2	2	00	...	...	...	...	...
5	...	...	...	0+	2+	<b>5</b>	3	1+	00	...	...	...	...
6	...	...	...	000	0+	2	2	0+	0	0+	...	...	...
7	...	...	...	...	0-	0	1	1	1	0	0+	...	...
8	...	...	...	...	...	0-	0-	1	?	0	0	0	...
9	...	...	...	...	...	00	00	0	...	...	00	00	...
10	...	...	...	...	...	...	...	...	...	0	...	...	...

on the intervals between adjacent rows and columns, the following equation is then obtained, capable of representing all the null-lines

to within the amounts given in the "Obs.-Calc." column of Table II:

$$\nu = 24234.17 + 1016.30 n' - 17.773 n'^2 + 0.410 n'^3 - 0.00487 n'^4 - 1145.00 n'' + 6.570 n''^2. \quad (4)$$

The comparatively large coefficients of the cubic and biquadratic terms in  $n'$  are unusual, but such terms are definitely needed to represent the data. The relationship between the coefficients of the initial and final states is of a normal type. Since null-lines and origins<sup>13</sup> are probably practically coincident for the SiN bands (cf. discussion preceding Eq. (2)), Eq. (4) should hold equally for both.

#### CONFIRMATION OF THE ISOTOPE EFFECT

For each observed Si<sup>29</sup>N and Si<sup>30</sup>N head, comparison is made in Table II of the observed isotopic displacement<sup>13</sup> with that theoretically calculable. For a given band-head, the displacement should be the sum of a small rotational part corresponding to the distance from band-origin to band-head, and a larger vibrational part corresponding to the distance from system-origin to band-origin.<sup>13</sup> The rotational displacement must in every case be negative, since the distance  $H$  (head minus origin, cf Eq. (2)) is positive in the SiN bands, and is less for the two heavier isotopes than for the lightest isotope Si<sup>28</sup>N with which the other two are compared. The vibrational displacement should also be negative on the high frequency side of the system-origin, with the result that in each band the Si<sup>29</sup>N and Si<sup>30</sup>N heads are superposed on the shading from the Si<sup>28</sup>N head and so escape detection. On the low-frequency side of the system-origin, however, the vibrational displacement is positive, so that, as soon as the effect of the small negative rotational displacement is overcome, the isotope heads stand out clearly on the high-frequency side of the Si<sup>28</sup>N head, where there is usually nothing to obscure them seriously. This can be seen in the reproductions (Plate I), where most of the heads of Table I are visible.

The rotational isotopic displacement for a given band can be determined by calculating  $H$  of Eq. (2) for Si<sup>28</sup>N and subtracting the result from the corresponding value for Si<sup>29</sup>N or Si<sup>30</sup>N. For Si<sup>28</sup>N, the values of  $B'$  and  $C$  used in calculating  $H$  are obtained from Eq. (3); for the other isotopes, the following equations (3') and (3'') must be used:

$$\begin{aligned} \text{Si}^{29}\text{N} : B' &= 0.7196 - 0.00953 n'; \\ C &= -0.01196 - 0.00953 n' + 0.00521 n'' \end{aligned} \quad (3')$$

$$\begin{aligned} \text{Si}^{30}\text{N} : B' &= 0.7118 - 0.00938 n'; \\ C &= -0.01183 - 0.00938 n' + 0.00512 n'' \end{aligned} \quad (3'')$$

The constant terms of (3') and (3'') are obtained<sup>13</sup> by multiplying the corresponding terms of Eq. (3) by  $\rho^2$ , and the coefficients of the  $n'$  and  $n''$  terms by multiplying the coefficients of Eq. (3) by  $\rho^3$ . In general  $\rho^2 = (1/M_2 + 1/M') / (1/M_1 + 1/M')$ . In the present case  $M' = 14$  (the atomic weight of N),  $M_1 = 28$ , and  $M_2$  is either 29 or 30. For  $\text{Si}^{29}\text{N}$ , the values of  $\rho$ ,  $\rho^2$ ,  $\rho^3$ , and  $\rho^4$  are as follows: 0.994236, 0.988505, 0.982808, and 0.977142; for  $\text{Si}^{30}\text{N}$ , they are 0.988826, 0.977777, 0.966852, and 0.956026.

The vibrational isotopic displacement for any band can be obtained in a similar way, using Eq. (4) for the  $\text{Si}^{28}\text{N}$  band, and subtracting the result from that obtained by Eq. (4') or (4'') for  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$ . Eqs. (4') and (4'') are obtained from (4) by multiplying each coefficient in the latter by a power of  $\rho$  equal to the power of  $n'$  or  $n''$  with which the coefficient is associated, the constant term being left unchanged since no electronic isotope effect is to be expected.<sup>13</sup>

$$\begin{aligned} \text{Si}^{29}\text{N} : \nu^0 &= 24,234.17 + 1010.44 n' - 17.569 n'^2 + 0.403 n'^3 \\ &\quad - 0.00476 n'^4 - 1138.40 n'' + 6.494 n''^2 \end{aligned} \quad (4')$$

$$\begin{aligned} \text{Si}^{30}\text{N} : \nu^0 &= 24,234.17 + 1004.96 n' - 17.394 n'^2 + 0.396 n'^3 \\ &\quad - 0.00466 n'^4 - 1132.21 n'' + 6.424 n''^2 \end{aligned} \quad (4'')$$

Practically, of course, equations obtained by subtracting (4) from (4') or (4''), respectively, are convenient in the calculation of vibrational isotopic displacements.

Comparison of observed with calculated isotopic displacements in Table II shows complete agreement, within experimental error, throughout the range of  $n'$  and  $n''$  values for which data could be obtained.<sup>15</sup> This thoroughgoing agreement seems the more remarkable when it is noted that each calculated isotopic displacement is the sum of a number of terms involving a variety of powers of  $\rho$ .<sup>16</sup> But such a detailed

<sup>15</sup> The apparent slight increase of the observed displacements relative to the calculated, as  $n'$  is increased, may be real but is within experimental error; note especially that the largest discrepancies are in the cases of the (7,7), (7,8) and (6,8) heads, which were the three weakest heads that were measurable. Also, the calculated displacements may be slightly in error due to inaccuracy in the coefficients of Eq. (4).

<sup>16</sup> The calculated values are considerably larger (especially for larger values of  $n$ , where the higher power terms in  $n$  have their greatest effect) than they would be if calculated according to the approximate relation<sup>13</sup> (which would be exact if there were no higher power terms)  $(\nu_2^n - \nu_1^n) = (\rho - 1)\nu_1^n$ ,  $\nu_1^n$  being the vibrational part of the emitted frequency for  $\text{Si}^{28}\text{N}$  (equal to wave-number for given band-origin minus that for system-origin). For example, the correct calculated vibrational displacement for the (7,7) band of  $\text{Si}^{30}\text{N}$  is 17.40, whereas the value obtained by the above approximate relation is  $(22914 - 24235)(-0.011174) = +14.76$ .

agreement, if any at all, is to be expected, since the theory is of such a nature that its detailed predictions in regard to the various coefficients all stand or fall together.<sup>17</sup>

The agreement of the observed with the calculated isotope effect is evidence against the possibility that half-integral quantum numbers ( $\frac{1}{2}$ ,  $1\frac{1}{2}$ ,  $2\frac{1}{2}$  . . . .) should have been employed instead of the integral numbers (0, 1, 2, . . . .) actually used in the calculation. If half-integral numbers were applicable, all the calculated values of Table II should be increased to approximately the mean of the given value and the value for the band having values of  $n'$  and  $n''$  both one unit greater; this increase amounts to about 0.8 units for  $\text{Si}^{29}\text{N}$  and 1.4 units for  $\text{Si}^{30}\text{N}$ . As a matter of fact, however, there are distinct indications<sup>15</sup> that there may be an effect of this sort masked by a small constant displacement in the other direction. The mean value of the observed minus calculated isotope effect is  $-0.1$  for  $\text{Si}^{29}\text{N}$  and  $+0.4$  for  $\text{Si}^{30}\text{N}$  (giving half weight to observed data marked doubtful, and omitting the value 31.2 for the 7,8 band). Adding 0.9 to all observed values would bring these averages to 0.8 and 1.3, respectively, which are very near the amounts 0.8 and 1.4 above calculated. Such a relative displacement in the measured, as compared with the true, interval between a  $\text{Si}^{29}\text{N}$  or  $\text{Si}^{30}\text{N}$  head and a corresponding  $\text{Si}^{28}\text{N}$  head is not inconceivable, in view of the enormous difference of intensity. Hence the question of half vibrational quantum numbers for SiN cannot be considered definitely settled in the negative. It should be further noted that the existence of integral quantum numbers here would be in contradiction to the probable close analogy of SiN to BO for which the evidence<sup>9</sup> is strongly in favor of the half-integral numbers.

The evidence of the isotope effect in favor of SiN as emitter of the present bands is more definite. The only compounds other than SiN whose theoretical isotopic displacements are at all near those observed are SiC and SiO. The former need not be considered; for the latter, the value of  $(\rho-1)$  is  $-0.00629$  for  $\text{Si}^{29}\text{O}$  and  $-0.01220$  for  $\text{Si}^{30}\text{O}$ . These are about 9 percent greater than the corresponding values for SiN; and the same is true for  $(\rho^2-1)$ ,  $(\rho^3-1)$ , etc., since, approximately,

<sup>17</sup> Although, of course, the observed agreement does not constitute a quantitative confirmation of theory for the small higher power terms, it does involve a close agreement for the linear and at least approximate agreement for the quadratic terms. An attempt to obtain equations for the  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$  heads directly from the experimental data (such a method was used in the case of  $\text{B}^{10}\text{O}$  and  $\text{B}^{11}\text{O}$ ) in order to compare the coefficients with those of Eq. (4) for  $\text{Si}^{28}\text{N}$ , would not have been of much value here, on account of the fewness of the data on the isotope heads.

$(\rho^2 - 1) = 2(\rho - 1)$ ,  $(\rho^3 - 1) = 3(\rho - 1)$ , etc. Hence, every term in (and so the total magnitude of) any calculated isotopic displacement, must be about 9 percent greater for SiO than for SiN. If one adds 9 percent to each of the calculated displacements of Table II, it is apparent that the agreement with the observed displacements becomes much poorer than at present.<sup>18</sup> This evidence in favor of SiN is strongly supported by the chemical evidence previously cited. The fact that the known SiO bands<sup>10</sup> are not obtained with the present bands and have no coefficients in common with those of the latter also supports the case against SiO as a possible emitter of the present bands.

#### INTENSITY DISTRIBUTION IN THE SiN BANDS

*Rotational distribution.* The reproductions show strikingly, especially for the bands belonging to the sequence for which  $\Delta n = 0$ , the rise in intensity in each branch from the null-line. In the negative branch, the intensity can be seen to rise rather rapidly to a maximum and then to fall slowly; in fact, irradiation at the end of the image of the slit on the plate has traced for each band a sort of flattened intensity distribution curve resembling that for a Maxwellian distribution. A similar rise to a maximum in the positive branch, followed by a fall before the head is reached, can be seen in the (0,0) and less clearly in the (1,1) band. Of course the apparent intensity distribution is greatly affected, especially in the positive branch, where also there is the overlap of lines returning from the head, by the changing spacing of the lines. A very rough estimate of the position of the most intense line in each branch, after attempting to discount the above effects, gives  $m_{max} = 13$ . For thermal equilibrium, this would correspond by the equation  $T = (1.431)(2B)m_{max}^2$  to a temperature of 80°C, a reasonable figure for the actual temperature, and similar to the result obtained by Birge in the case of the CN bands generated in active nitrogen.<sup>3</sup>

*Vibrational distribution.* As in the cases of BO and CN, the low effective temperature indicated by the rotational quantum number distribution is belied by the vibrational energy distribution. Instead of the very rapid fall of intensity from intense bands with  $n' = 0$  to very weak bands with  $n' = 1$  and undetectable intensity for higher  $n'$  values, the summed emission intensity actually rises from  $n' = 0$  until  $n' = 3$ , and then falls gradually (cf Fig. 1). This type of phenomenon

<sup>18</sup> It should be noted that the effect of substituting half-quantum numbers, and that of substituting SiO for SiN, *both* would produce an *increase* of the calculated isotopic displacements, so that there is no possibility of a mutual cancellation of the two effects.



has been discussed in previous papers<sup>19,20</sup> on BO and on CuI, to which reference should be made.

The intensity distribution with respect to observed values of  $\Delta n$  appears to be very similar to that in the violet CN bands,<sup>21</sup> and of a type indicating, according to Lenz's theory, that the motion of the excited electron is unusually little affected by the vibration of the molecule. The sequence  $\Delta n = 0$  is by far the most intense,  $\pm 1$  are fairly strong, while  $+2$ ,  $-2$ ,  $+3$ ,  $-3$ , and  $+4$  (the last represented only by one weak head, which may be spurious) follow in diminishing order of intensity. In spite of the restricted range of  $\Delta n$  values as compared with cases such as BO and CuI, two relations found to hold for the latter<sup>19,20</sup> are also clearly present in the SiN bands. These are a preference for positive over negative  $\Delta n$  values, and a tendency, also noted in several additional cases by Birge,<sup>20</sup> for the numerically larger  $\Delta n$  values to be associated with the larger values of  $n'$ . The general preponderance of intensity in Table III on the positive side of the diagonal drawn through the members of the sequence  $\Delta n = 0$ , shows the existence of the first relation. The second is shown by the increasing length of the rows of figures in Table III as  $n'$  increases; particular attention may be called to the low intensity of the bands (1,0), (2,0), and (0,1), (1,2), (0,2), (1,3), the last four not having been found at all.<sup>22</sup> An explanation of these effects in terms of Lenz's theory has been given in the paper on CuI.<sup>20</sup>

#### NEW SYSTEM OF BANDS IN THE SILICON NITRIDE SPECTRUM

In addition to the intense system of SiN bands discussed above, which for convenience will in the following be called the A bands of SiN, a number of additional, but very much weaker bands, are

<sup>19</sup> See ref. 9, p. 292-3, (BO).

<sup>20</sup> See ref. 8, pp. 20-24, (CuI); also abstract of paper by R. T. Birge, *Phys. Rev.* **25**, 240 (1925), in regard to  $n'$  and  $\Delta n$  distribution.

<sup>21</sup> The resemblance is well brought out when the CN bands are obtained by the action of active nitrogen on carbon compounds. In the violet CN bands, the dominance of the sequence  $\Delta n = 0$  and the tendency toward the restriction of  $\Delta n$  to small values are much as in the SiN bands, but perhaps somewhat less marked. Although the violet CN bands are shaded toward the violet, not toward the red like the SiN bands, this difference is a superficial one from the theoretical standpoint, being due to the fact that the coefficient  $C$  has small positive values in the first case and small negative values in the second case.

<sup>22</sup> This is partly due to the weakness of the heads of these bands, due to their large (calculated) distance from the null-lines in this region. But if the bands had been at all intense, the region of maximum intensity on either side of the null-line would certainly have been seen.

TABLE IV

Wave-number data on heads of new bands.

Heads marked "masked" are concealed usually by bands of the more intense SiN system. Heads marked \* appear only as emphasized structure lines of a SiN or NO band; in the case of those marked †, two heads fall together; those marked ? are of doubtful identity as members of the system.

Wave-numbers for  $n'=7$ ,  $n''=0$  should be added to the Table. They are 31372 and 31348.

$n'' \rightarrow$	0	1	2	3	4	5	6
0	.....	.....	28050*678	28728 673	29401 664	30065 657	30722 650
↓	.....	.....	28017*682	28699 674	29373 665	30038 659	30697 651
			1019	1018	1021	1022	1020
			1012	1017	1019	1020	1027
1	.....	26348†683	27031 679	27710 670	28380 663	29043 659	29702*
	.....	26318 687	27005 677	27682 672	28354 664	29018 652	29670*
		1005	1008	1009	1009	1008	
			1004	1010	1010	1014	
2	.....	25343 680	26023 678	26701 670	27371 664	28035*	
	.....	Masked	26001*671	26672 672	27344 660	28004*	
		1001	997		998		
					996		
3	.....	24342 684	25026	Absent	26373	.....	.....
	.....	24318	Absent	Absent	26348*	.....	.....
					979		
					978		
4	Masked	.....	.....	Absent?	25394	.....	.....
	22649	.....	.....	Absent	25370	.....	.....
5	.....	21708 691	22397 689	23086	Masked	.....	.....
	.....	21679 691	22370 688	23058 681	23739?	.....	.....
6	.....	21439	Absent or	22802 668	23470*	.....	.....
	.....	21412	Masked	Masked	23438*	.....	.....
7	19804 692	20496 685	21181 684	21865?662	22527	Absent or	.....
	19784 685	20469 685	21154 679	21833?	Masked	Masked	.....
8	18873†689	19562 686	20248 679	20927	Absent or	.....	.....
	18849†690	19539 679	20218 677	20895	Masked	.....	.....
9	.....	18639?688	19327		20678	.....	.....
	.....	18608*?695	19303 679	19982 674	20656	.....	.....
10	.....	.....	18416 681	19097 671	19768	.....	.....
	.....	.....	18931*681	19072	.....	.....	.....
11	.....	.....	.....	18203 670	18873†	.....	.....
	.....	.....	.....	18177 672	18849†	.....	.....
12	.....	.....	.....	.....	17996	.....	.....
	.....	.....	.....	.....	17969	.....	.....
13	.....	.....	.....	.....	.....	[663]17793	.....
	.....	.....	.....	.....	.....	[663]17768	.....

present. Their presence is obvious only in the near ultraviolet and in the green, but on careful examination it was found that they extend through the intervening region and belong to a single system. They are all shaded toward the red, and in the ultraviolet, where conditions are most favorable, are seen to become resolved, at a moderate distance from the head, into a series of structure lines. The heads are in pairs of about equal intensity, with a separation averaging 26.8 wave-number units and apparently constant or nearly so.

Measurements, of no great accuracy, were made on the heads of the new bands in the hope of finding possible relations between them and the A bands. The wave-number data are given in Table IV, and the intensities in Table V. The former are so arranged as to show the

TABLE V

*Intensity distribution in new bands (estimated photographic intensities). Vacant spaces represent bands not found; a few of these may be weakly present but masked by heads of the more intense SiN system.*

$n'' \rightarrow$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
$n' \downarrow$ 0	...	...	...	...	00	0	...	0-	0+	...	...	...	...	...
1	...	0-	0	0-	...	1	0+	1	0-	0+?	...	...	...	...
2	00	1-	1-	(2)	...	0	...	0+	1	2+	0	...	...	...
3	0-	1	1	...	...	0?	0+	0?	0	0	1+	1	...	...
4	1-	2-	0	0-	0	...	1-	0	...	1	00	0+	1	...
5	0	0	00	...	...	...	...	...	...	...	...	...	...	0
6	0-	000	...	...	...	...	...	...	...	...	...	...	...	...
7	00	...	...	...	...	...	...	...	...	...	...	...	...	...

constant differences between adjacent rows and columns which is the basis of the assignment of vibrational quantum numbers made. On account of the peculiar intensity distribution, the absolute numbering is somewhat uncertain in respect to  $n'$ , but is quite definite in regard to  $n''$ , since there is no indication of additional bands in the ultraviolet beyond the relatively intense series for which  $n'' = 0$ . The positions of the heads of the new bands can be represented approximately (a systematic analysis to determine the best values of the coefficients has not been made) by the equation:

$$\nu = \left\{ \begin{array}{l} 26676 \\ 26649 \end{array} \right\} + 694n' - 3.3n'^2 - 1025.9n'' + 6.4n''^2. \quad (5)$$

From a comparison of Eqs. (4) and (5) it is evident that the new bands have no term in common with the A bands. Although the new bands are presumably due to SiN, there is no definite proof of this from the isotope effect; but this could not have been expected, on account of the low intensity of the bands even in the most intense exposures.

Observations on the new bands showed them to be quenched in the same manner as the A bands by small amounts of oxygen. This indicates that they are due to the same emitter. Also, the numerical values of the coefficients and the spacing of the structure lines are of the same order of magnitude as for the A bands. It is possible, of course, that the new bands are not due to SiN, but to some other diatomic emitter such as Si<sub>2</sub> or SiP. SiCl must be ruled out, since the relative abundance of the isotopes of chlorine is such that both SiCl<sup>35</sup> and SiCl<sup>37</sup> heads should have been visible even with the low intensities used.<sup>23</sup>

TABLE VI  
*Unidentified heads or lines in SiN spectrum.*

Wave-No.	Type	Int.	Wave-No.	Type	Int.	Wave-No.	Type	Int.
24267		1	22777	v	3-	21088		1d
149	l?	0	745	v	3-	071		1d
23989	l?	3	446	v?	0	20816	l?	0
960		0	423	v?	0+	773	r	0-d
871	1	0+	016	v	1+	736	r	0-d
836	1	1+	21970	l?	*0+	146	v?	00
712		0	963	l?	*0+	142	v?	00
232	l?	1+	925	v?	1-	19993	r	00
176	l?	1	914	v?	0+			
22997	l?	3	822	v?	1			
985	l?	3-	818		0			
970	v?	2+	800	v?	1			
949	v?	1	797		0			
894	v	3	715	l?	1-			
870	v	3	291	v?				

Notes: 1 = line; v = shaded toward violet; r = shaded toward red; d = diffuse; \* means superposed on structure line.

The intensity distribution (cf Table V) in the new bands is of an interesting type characterized by a preference for numerically large  $\Delta n$  values, and by the non-occurrence of the band (0→0) and neighboring bands. This distribution approaches that typified by the visible iodine bands.<sup>24</sup> It indicates that the motion of the emitting electron is very markedly affected by the vibration of the molecule.—It should be stated that Tables IV and V include all bands of appreciable intensity, except possibly at the extreme red end.

From the analogy of SiN to CN one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. No such bands were found, presumably because they lie too far in the infrared. Possibly the new SiN system has for its final electronic state a doublet state identical with the initial state of the hypothetical red SiN bands. In

<sup>23</sup> Also, these bands have not been reported by Jevons (Proc. Roy. Soc. **106A**, 174, 1924) in his investigation of the discharge through pure SiCl<sub>4</sub> vapor.

<sup>24</sup> Cf refs. 12 and Birge, ref. 20; and especially R. Mecke, Phys. Zeits. **26**, 234 (1925).

addition to the new bands and the A bands, there are a number of unidentified lines or heads; the data are given in Table VI. Some of these are rather intense, and many are shaded toward the violet; it is possible that these last will prove of importance in the spectrum of SiN.

The writer wishes to express his gratitude to Prof. G. P. Baxter of the Chemistry Department for the pure SiCl<sub>4</sub> used in the above work.

JEFFERSON PHYSICAL LABORATORY,  
HARVARD UNIVERSITY,  
June 5, 1925

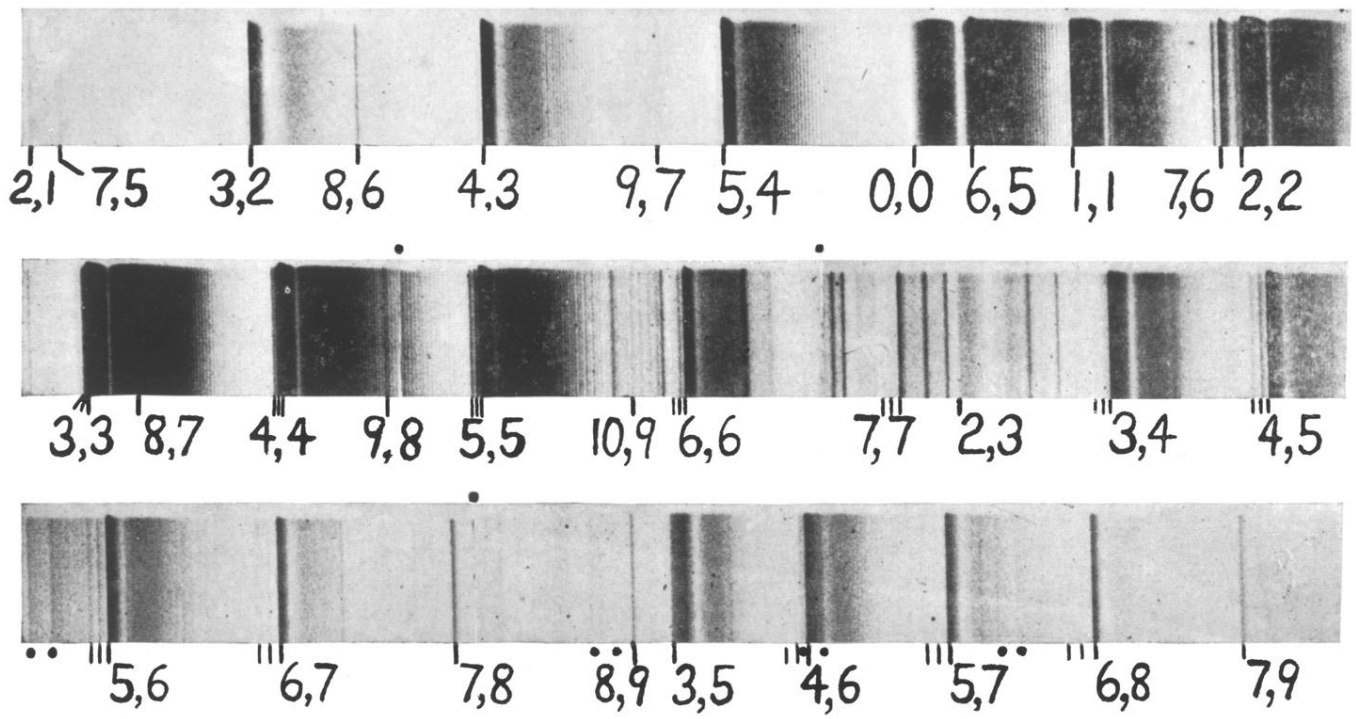


PLATE 1. The entire band spectrum of SiN from  $\lambda 3986$  (top) to  $\lambda 4800$  (bottom).