Rotational Analysis of Ultraviolet Bands of Silicon Monoxide

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From measurements on silicon arc spectrograms a rotational analysis has been made of the (0,1), (0,2), (0,3), (0,4) and (1,4) bands of the ultraviolet band system of silicon monoxide (SiO). The bands were found to be due to a $^1\Pi\rightarrow{}^1\Sigma$ transition as was expected by analogy with the fourth positive bands of CO. Among the constants obtained from the analysis are

$$B_0'=0.6270 \qquad r_e'=1.62\times10^{-8}\text{ cm} \qquad \alpha'=0.00657$$

$$B_0''=0.7238 \qquad r_e''=1.51\times10^{-8}\text{ cm} \qquad \alpha''=0.00494$$

A number of perturbations of the Q branch lines were observed. Some conclusions were reached as to the nature of the perturbing levels. From measurements of band heads of this system made by Jevons and the results of the present analysis the following equation was obtained for the band origins:

$$\begin{aligned}\nu_0 = 42835.3&+851.51(v'+1/2)-6.143(v'+1/2)^2+\\ &0.0437(v'+1/2)^3-1242.03(v''+1/2)+\\ &6.047(v''+1/2)^2-0.00329(v''+1/2)^3.\end{aligned}$$

Introduction

The ultraviolet band system of silicon monoxide (SiO) has heads, as listed by Jevons,[1] extending from 2176.6A to 2925.3A. The bands are shaded toward longer wave-lengths. According to Cameron,[2] these bands might be the analog of the fourth positive bands of CO. If so, they must be of the type $^1\Pi\rightarrow{}^1\Sigma$.

The writer has now made a rotational analysis of the (0,1), (0,2), (0,3), (0,4) and (1,4) bands. The analysis confirms the idea that they are $^1\Pi\rightarrow{}^1\Sigma$. Each band was found to consist of one P, one Q and one R branch.

Spectrograms

Using as a source a carbon arc with SiO_2 placed in the lower (positive) carbon, the writer photographed these bands in the first and second orders of a twenty-one foot concave grating. The iron arc was used as a comparison spectrum. Measurements of the (0,1) and some other bands were made from the spectrograms thus obtained in the second order, and the (0,1) band was partly analyzed. Then measurements were made of the (0,1), (0,2), (0,3), (0,4) and (1,4) bands from plates of silicon arc spectrograms, which Professor R. S. Mulliken received through the kindness of Professor W. F. C. Ferguson of New York University. The exposures were made by Professor Ferguson with the new, very large Hilger quartz spectrograph at the Bureau of Standards. The iron arc served as a comparison spectrum on these plates. The

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[1] W. Jevons, Proc. Roy. Soc. London **106,** 174 (1924).

[2] W. H. B. Cameron, Phil. Mag. (7) **3,** 110 (1927).

iron arc wave-lengths which were used were from those measured by K. Burns and F. M. Walters, Jr.[3] The quartz spectrograph plates just mentioned showed a dispersion, at 2500A, of about 0.874A/mm, as compared with about 1.24A/mm for the grating second order plates, and also showed a greater resolution than the grating plates. From measurements on these quartz spectrograph plates the five bands mentioned above were analyzed.

ROTATIONAL ANALYSIS

As the bands were excited at high temperature the series were long, and there was some overlapping of series lines from one band to another. Many of the observed lines were blends, and there were a number of atomic lines in the spectrum. The (0,1) band was analyzed first. The Q branch lines could be distinguished from the other series lines because of their greater intensity. The R branch lines near the origin were considerably stronger than the P branch lines in this region. Members of the P, Q and R series with common values of the rotational quantum number of the lower energy state were selected from these series with the aid of the relation

$$R(J) - Q(J) \cong Q(J+1) - P(J+1). \tag{1}$$

According to the quantum theory of band spectra, there is Λ-type doubling in a $^1\Pi$ state; each rotational level of this electronic state is double (c and d sets of sub-levels[4]). The Q lines are due to transitions from a different set of sub-levels of the $^1\Pi$ state than those from which the P and R lines originate. As a result there is a "combination defect" equal to $[R(J)-Q(J)]-[Q(J+1)-P(J+1)]$. In the case of these SiO bands this defect was found to be relatively small compared to the quantities $[R(J)-Q(J)]$ or $[Q(J+1)-P(J+1)]$ themselves.

In order to assign correctly the absolute J'' values the following relations were used:

$$\Delta_2T'(J) = R(J) - P(J) = 4B'(J+\tfrac{1}{2}) + 8D'(J+\tfrac{1}{2})^3 + \cdots \tag{2}$$

$$\begin{aligned}\Delta_2T''(J) &= R(J-1) - P(J+1) \\ &= 4B''(J+\tfrac{1}{2}) + 8D''(J+\tfrac{1}{2})^3 + \cdots .\end{aligned} \tag{3}$$

These relations were also used to calculate the constants B' and B''. The values of $[R(J)-P(J)]$ were plotted against successive integers. For relatively small values of J'' these points lay very approximately on a straight line and then with increasing J'' they began to deviate slightly from the line. A straight line was drawn through the points up to where they began to deviate. The slope of this line gave a good approximation to the value of $4B'$. Similarly, by plotting the values of $[R(J-1)-P(J+1)]$ against successive integers a good approximation to $4B''$ was obtained. Then D' and D'' were calculated with the aid of the theoretical relation

$$D_e = -4B_e^3/\omega_e^2, \tag{4}$$

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[3] K. Burns and F. M. Walters, Jr., Publications of the Allegheny Observatory of the University of Pittsburgh, Vol. VIII, No. 4.

[4] R. S. Mulliken, Rev. Mod. Phys. 3, 89 (1931).

neglecting the difference between D_e and D_v. The values of ω_e' and ω_e'' were obtained from the vibrational analysis of SiO made by Jevons,[1] from measurements on the heads of the bands. It was found that when the quantity $[R(J)-P(J)-8D'(J+1/2)^3]$ was plotted against successive integers, the points now all lay very approximately on a straight line, showing that there was no need of considering terms of higher power than the third to represent $\Delta_2T'(J)$. A similar statement holds for $\Delta_2T''(J)$. Thus by successive approximations and least squares the values of B' and B'' were obtained for the five bands analyzed. The values of B_0' as thus obtained from the analysis of the (0,1), (0,2), (0,3) and (0,4) bands agreed to within one-tenth of one percent or less. The values of B_1'', B_2'', B_3'' and B_4'' showed a very approximately linear variation according to the formula

$$B_v = B_0 - \alpha v. \tag{5}$$

The wave numbers of the P, Q and R lines, together with the rotational quantum numbers assigned to them, are listed in Table I. There are a number of perturbations of the Q branch lines. Their significance will be considered in a later section.

TABLE I.

The first six numbers give the wave number of the line considered. The seventh number, in bold-face type, expresses the estimated relative intensity of the line. Blends of two or more lines are indicated by an asterisk (*). The letter A indicates that a heavy atomic line is superposed on a band line.

	(0,1) band				(0,2) band	
P	*Q*	*R*	*J''*	*P*	*Q*	*R*
	41392.7**4**		14		40174.5**6**	
	89.7**4**		15		71.9**8***	
	86.6**6**		16		68.9**4**	
	83.0**4**		17		66.1**6**	
	79.3**6***		18		62.9**6**	
	75.7**6***		19		59.7**9***	
	71.9**6***		20		56.2**6**	
	67.9**8***		21	40126.4**4**	52.6A*	
	63.9**6**		22	21.5**4**	48.8**6**	
	59.7**6***		23	15.8**4**	44.9**6**	
	55.4**6***		24	10.4**4**	40.5**6**	
	50.7**6***		25	04.6**4**	36.0**6***	40167.5**3**
	45.8**6***		26	40099.1**5**	31.3**8***	64.6**2**
	40.9**8***		27	92.9**3**	26.7**6***	61.6**4**
41300.4**6***	35.7**6***	41371.9**6***	28	86.7**4**	22.1**6***	58.0**6**
41293.8**6***	30.5**6***	67.9**8***	29	80.3**3**	17.0**8***	54.1**4**
87.1**3**	24.8**6***	63.5**4**	30	73.8**5**	11.8**8***	50.3**4**
80.3**3**	19.0**6***	58.7**8***	31	67.2**4**	06.0**8***	46.0**4**
73.2**2**	13.0**6***	54.1**4**	32	60.6**9***	00.4**8***	41.5**4**
65.7**3**	06.8**6***	49.0**4**	33	53.3**4**	40094.4**8***	36.0**6***
57.9**3**	00.4**6***	43.9**6**	34	46.1**9***	88.8**9***	31.8**8***
50.0**3**	41293.8**6***	38.3**6**	35	38.8**9***	82.5**8**	26.7**6***
42.1**3**	88.0**6**	33.7**4**	36	31.2**8***	76.8**8**	22.1**6***
34.8**3**	80.7**6**	28.1**4**	37	24.2**8***	70.0**6**	17.0**8***
26.1**3**	73.6**6**	22.2**4**	38	15.5**8***	63.1**6**	11.8**8***
17.5**3**	66.2**6**	15.8**4**	39	07.5**6***	56.4**6**	06.0**8***
08.8**3**	58.6**6**	09.6**4**	40	39999.2**6***	49.1**6**	00.4**8***
00.1**3**	51.1**6**	03.2**4**	41	90.7**8***	42.0**6**	40094.4**8***
41191.0**3**	43.2**6**	41296.5**4**	42	82.1**6***	34.5**6**	87.9**9***
81.5**3**	35.2**6**	89.7**4**	43	72.8**6***	26.9**6**	81.8**4**

TABLE I. (*Continued*).

	(0, 1) band				(0, 2) band	
P	*Q*	*R*	*J''*	*P*	*Q*	*R*
72.03	27.06	82.84	44	64.64	19.26	75.04
62.43	18.66	75.74	45	55.16	11.36	68.34
52.63	09.96	68.44	46	45.64	03.16	61.39*
42.63	01.26	60.64	47	36.14	39994.66	53.94
32.43	41192.28*	52.64	48	26.24	86.16	46.19*
22.03	82.86	44.64	49	16.34	77.56	38.89*
11.53	73.68*	36.54	50	06.34	68.66	31.28*
00.66*	63.98*	27.94	51	39896.04	59.56	24.28*
41089.56*	54.18*	19.64	52	85.84	50.36	15.58*
78.36*	44.08*	10.84	53	75.2A*	40.86	07.56*
66.76*	34.06	01.54	54	63.94	31.16	39999.26*
54.96*	23.66	41192.28*	55	53.04	21.26	90.78*
43.23	13.06	84.04	56	41.84	11.36	82.16*
31.53	02.36	73.68*	57	30.28*	01.06	72.86*
20.04	41091.26	63.98*	58	19.52	39890.65	63.34
06.94	80.06	54.18*	59	07.34	80.1A*	54.04
40994.24	41068.76	41144.08*	60	39795.14	39869.35	39944.24
81.44	56.66	33.34	61	82.64	58.15	34.44
68.64	45.86	22.54	62		47.65	24.54
55.54	33.46	11.74	63		36.05	14.14
42.04	21.26	00.66*	64		24.25	03.94
28.35	08.86	41089.56*	65		12.64	39893.24
14.7A*	40996.16	78.36*	66		00.85	82.94
00.25	83.26	66.76*	67		39788.75	71.94
40886.74	70.16	54.96*	68			61.96*
72.24	57.16	42.84	69			49.34
57.54	43.66	30.44	70			37.63
42.57*	29.96	18.06	71			26.04
27.84	16.36	05.36	72			
12.63	02.16	40991.7A*	73			
40797.13	40887.96	79.26	74			
81.73	73.46	66.05	75			
65.83	58.55	52.55	76			
49.63	42.57*	38.65	77			
33.55*	29.65	24.95	78			
16.83	13.95	10.64	79			
00.45*	40798.15	40896.34	80			
40683.35*	82.35	81.64	81			
66.15*	66.44	66.83	82			
48.75*	50.04	51.53	83			
30.95*	33.55*	37.53	84			
13.15*		21.03	85			
		05.63	86			
		40789.53	87			
		73.33	88			
		57.13	89			
		40.33	90			
		23.53	91			

TABLE I. (*Continued*).

	(0,3) band				(1,4) band	
P	*Q*	*R*	*J''*	*P*	*Q*	*R*
	38980.56*		7			
	79.54*		8			
	78.54*		9			
	77.04*		10			
	75.99*		11			
	74.08*		12			

Table I. (*Continued*).

	(0, 3) band				(1, 4) band	
P	*Q*	*R*	J''	*P*	*Q*	*R*
	71.59*		13		38617.22	
	69.44*		14		15.11	
	67.04*		15		12.53	
	64.54*		16		10.04*	
	61.48*		17		07.36*	
	58.76*		18		03.94*	
	55.79*		19		00.96*	38625.34
	52.29*		20		38597.63	23.23
	48.79*	38974.08*	21		93.95	21.22
	45.29*	72.19*	22		90.24	18.64
	41.56*	69.44*	23	38558.33	86.44	16.01
	37.56	67.04*	24	52.83	82.53	13.23
	33.36	64.54*	25	47.26*	78.43	10.04*
	29.19*	62.44	26	41.51	73.93	07.36*
38890.88*	24.56	59.44	27	35.72	69.23	03.94*
85.06*	19.99*	56.39*	28	30.04*	64.54	00.36*
78.97*	15.24	52.29*	29	23.82	59.86	38596.62
72.56*	10.39*	48.79*	30	17.42	54.74	92.82
66.16*	05.06	45.29*	31	11.14*	49.43	88.83
59.56*	38899.86	40.94	32	04.41	43.82	84.73
52.86*	94.38	36.25	33	38497.84	38.66*	80.42
46.14	88.56	31.75	34	90.64*	32.76*	75.43
38.94	83.85	28.04	35	83.64*	26.83	70.72
31.64	77.56	23.14	36	76.14*	20.72	66.03
25.15*	71.16	18.79*	37	68.53	14.59*	61.24*
17.06*	64.66	13.09*	38	60.93	07.94*	55.83
09.44	58.16	07.78*	39	53.44	01.26*	50.56*
01.36*	51.46	02.39*	40	45.13	38494.64*	45.24
38793.54	44.76	38896.69*	41	37.04	87.54*	39.06*
85.34	37.56	90.88*	42	29.04	80.34*	33.26*
76.94	30.56	85.06*	43	19.84	73.03*	27.82
68.14	23.26*	78.97*	44	11.63	66.13	21.42
59.44	15.69*	72.56*	45	03.14*	58.69*	14.59*
50.54	07.96*	66.16*	46	38393.93	50.53	07.94*
41.44	38799.99*	59.56*	47	84.43	42.86	01.26*
32.04	92.06*	52.86*	48	75.04*	33.53	38494.64*
22.75	83.86	45.44	49	65.38*	25.34	87.54*
13.14	75.36	38.34	50	55.53	17.84	80.34*
03.44	66.86	31.14	51	45.93	08.94	73.03*
38693.24	58.16	23.26*	52	36.74*	00.86*	65.64
83.15	49.16	15.69*	53	26.14*	38391.23	57.92
72.95	40.06	07.96*	54	15.64*	81.86*	48.54
38662.44	38730.76	38799.99*	55	38304.63*	38371.76	38440.13
51.74	21.26	92.06*	56	38293.64*	62.26	31.73
40.85*	11.66	83.04	57	82.66*	52.26	22.94
	01.86	74.44	58		42.25	14.03
	38691.86	65.74	59		32.06	05.23
	81.46	56.64	60		21.76	38396.34
	70.96	47.64	61		10.96	86.44
		38.24	62		00.25	77.04
		28.55	63		38289.46	67.63
		19.05	64			57.13
		08.65	65			47.13
		38699.15	66			36.74*
		88.65	67			26.14*
		78.22	68			15.64*
		67.35	69			04.63*
		56.64	70			38293.64*
		45.64	71			82.66*

TABLE I. (*Continued*).

J''	(0,4) band P	Q	R	J''	(0,4) band P	Q	R
11		37782.53		43	37592.03	45.74	00.44*
12		80.83		44	83.93	38.94	37694.75*
13		78.73		45	75.72	31.74	89.14*
14		76.62		46	67.23	24.74	82.94*
15		74.34		47	58.73	17.24	76.62
16		71.83*		48	49.64*	09.64	70.23
17		69.14*		49	40.93	01.94	63.64
18		66.36*		50	31.93	37594.36	57.03
19		63.53		51	22.63	86.05	50.13
20		60.66*		52	13.13	77.75	43.44*
21		57.26*		53	03.53	69.45	36.63
22		53.73		54	37493.83	60.85	28.83
23		50.13		55	83.73	52.04	21.03
24		46.53		56	73.83*	43.14	14.12
25		42.54		57	37463.43	37534.24	37605.63
26		38.44	37771.83*	58		25.04	37597.63
27	37700.44*	34.23	69.14*	59		15.54	89.43
28	37694.75*	30.14*	66.36*	60		05.94	81.43
29	89.14*	25.43	63.01	61		37496.04	72.44
30	82.94*	20.83	59.44*	62		86.65	63.63
31	77.23	15.94*	55.83	63		76.43	54.63
32	70.82	11.04*	52.02	64		66.14	45.63
33	64.52	05.94*	48.13	65		56.09*	36.03
34	57.93	00.44*	43.93	66		45.16*	27.23
35	51.22	37694.75*	39.43	67		34.16*	17.74*
36	44.33*	89.94	35.63	68		23.46*	07.73
37	38.13	84.14	31.04	69			37497.73
38	30.43	77.94	26.33	70			87.43
39	23.13	71.84	21.33	71			77.32
40	15.63	65.63	16.44*	72			66.94
41	07.93	59.14	11.04*	73			56.09*
42	00.22	52.54	05.94*				

In Tables IIA and IIB, there are listed agreements in the combination differences.

TABLE IIA. *Agreements in the combination differences.*

Note (1): $R(J)-Q(J+1)$ should not necessarily be exactly the same for the (0,4) and (1,4) bands, since the Λ-type doublet widths are not necessarily the same, for given J values, for $v'=0$ and $v'=1$.

Note (2): In some of the bands, additional combination differences are available, but are omitted from the table because of the absence of comparison data from other bands.

J	$R(J)-Q(J)=T'(J+1)-T'(J)+\Delta\nu_{dc}'(J)$ (0,1)	(0,2)	(0,3)	(0,4)	$R(J)-Q(J+1)=T''(J+1)-T''(J)+\Delta\nu_{dc}'(J+1)$ (0,4)	(1,4)
25		31.5	31.2			
26		33.3	33.3	33.4	37.6	38.1
27		34.9	34.9	34.9	39.0	39.4
28	36.2	35.9	36.4	36.2	40.9	40.5
29	37.4	37.1	37.0	37.6	42.2	41.9
30	38.7	38.5	38.4	38.6	43.5	43.4
31	39.7	40.0	40.2	39.9	44.8	45.0
32	41.1	41.1	41.1	41.0	46.1	46.1
33	42.2	41.6	41.9	42.2	47.7	47.7
34	43.5	43.0	43.2	43.5	49.2	48.6
35	44.5	44.2	44.2	44.7	49.5	50.0
36	45.7	45.3	45.6	45.7	51.5	51.5

TABLE IIA. (*Continued*)

J	$R(J)-Q(J)=T'(J+1)-T'(J)+\Delta\nu_{dc}'(J)$				$R(J)-Q(J+1)=T''(J+1)-T''(J)+\Delta\nu_{dc}'(J+1)$	
	(0,1)	(0,2)	(0,3)	(0,4)	(0,4)	(1,4)
37	47.4	47.0	47.6	46.9	53.1	53.3
38	48.6	48.7	48.4	48.4	54.5	54.6
39	49.6	49.6	49.6	49.5	55.7	55.9
40	51.0	51.3	50.9	50.8	57.3	57.7
41	52.1	52.4	51.9	51.9	58.5	58.7
42	53.3	53.4	53.3	53.4	60.2	60.2
43	54.5	54.9	54.5	54.7	61.5	61.7
44	55.8	55.8	55.7	55.8	63.0	62.8
45	57.1	57.0	56.9	57.4	64.4	64.0
46	58.5	58.2	58.2	58.2	65.7	65.1
47	59.4	59.3	59.6	59.4	67.0	67.7
48	60.4	60.0	60.8	60.6	68.3	69.3
49	61.8	61.3	61.6	61.7	69.3	69.7
50	62.9	62.6	63.0	62.7	71.0	71.4
51	64.0	64.7	64.3	64.1	72.4	72.2
52	65.5	65.2	65.1	65.7	74.0	74.4
53	66.8	66.7	66.5	67.2	75.8	76.1
54	67.5	68.1	67.9	68.0	76.8	76.8
55	68.6	69.5	69.2	69.0	77.9	77.9
56	71.0	70.8	70.8	71.0	79.9	79.5
57	71.3	71.8	71.4	71.4	80.6	80.7
58	72.7	72.7	72.6	72.6	82.1	82.0
59	74.1	73.9	73.9	73.9	83.5	83.5
60	75.3	74.9	75.2	75.5	85.4	85.4
61	76.7	76.3	76.7	76.4	85.8	86.2
62	76.7	76.9		77.0	87.2	87.6
63	78.3	78.1		78.2		
64	79.4	79.7		79.5		
65	80.7	80.6		80.0		
66	82.2	82.1		82.1		
67	83.5	83.2		83.6		
68	84.8			84.3		

TABLE IIB. *Agreements in the combination differences.*

J	$R(J)-P(J)=\Delta_2T'(J)$				$R(J-1)-P(J+1)=\Delta_2T''(J)$	
	(0,1)	(0,2)	(0,3)	(0,4)	(0,4)	(1,4)
27		68.7	68.6	68.7	77.1	77.3
28	71.5	71.3	71.3	71.6	80.0	80.1
29	74.1	73.8	73.3	73.9	83.4	82.9
30	76.4	76.5	76.2	76.5	85.8	85.5
31	78.4	78.8	79.1	78.6	88.6	88.4
32	80.9	80.9	81.4	81.2	91.3	91.0
33	83.3	82.7	83.4	83.6	94.1	94.1
34	86.0	85.7	85.6	86.0	96.9	96.8
35	88.3	87.9	89.1	88.2	99.6	99.3
36	91.6	90.9	91.5	91.3	101.3	102.2
37	93.3	92.8	93.6	92.9	105.2	105.1
38	96.1	96.3	96.0	95.9	107.9	107.8
39	98.3	98.5	98.3	98.2	110.7	110.7
40	100.8	101.2	101.0	100.8	113.4	113.5
41	103.1	103.7	103.1	103.1	116.2	116.2
42	105.5	105.8	105.5	105.7	119.0	119.2
43	108.2	109.0	108.1	108.4	122.0	121.6
44	110.8	110.4	110.8	110.8	124.7	124.7
45	113.3	113.2	113.1	113.4	127.5	127.5
46	115.8	115.7	115.6	115.7	130.4	130.1

Table IIB. (*Continued*).

J	$R(J)-P(J)=\Delta_2T'(J)$				$R(J-1)-P(J+1)=\Delta_2T''(J)$	
	(0,1)	(0,2)	(0,3)	(0,4)	(0,4)	(1,4)
47	118.0	117.8	118.1	117.9	133.3	132.9
48	120.2	119.9	120.8	120.6	135.7	135.9
49	122.6	122.5	122.7	122.7	138.3	139.1
50	125.0	124.9	125.2	125.1	141.0	141.6
51	127.3	128.2	127.7	127.5	143.9	143.6
52	130.1	129.7	130.0	130.3	146.6	146.9
53	132.5	132.3	132.5	133.1	149.6	150.0
54	134.8	135.3	135.0	135.0	152.9	153.3
55	137.3	137.7	137.5	137.3	155.0	154.9
56	140.8	140.3	140.3	140.3	157.6	157.5
57	142.1	142.6	142.2	142.2		
58	143.9	143.8				
59	147.2	146.7				
60	149.8	149.1				
61	151.9	151.8				

Λ-type Doubling

The combination defects in the (0,1), (0,2), (0,3) and (0,4) bands were computed for each value of J and, where possible, averaged over the different bands. The definition of $\Delta\nu$ (in cm^{-1}) for Λ-type doubling,[5] which will be used here is

$$\Delta\nu_{dc}(J) = T_d(J) - T_c(J). \tag{6}$$

For a $^1\Pi$ state,[5] according to Van Vleck, one expects theoretically

$$\begin{aligned} T_d(J) &= T_0 + B_vJ(J+1) - 2C + (C+C_1)J(J+1) + \cdots ; \\ T_c(J) &= T_0 + B_vJ(J+1) - 2C + (C+C_2)J(J+1) + \cdots . \end{aligned} \tag{7}$$

$$\begin{aligned} \Delta\nu_{dc}(J) &= qJ(J+1), \text{ where } q = C_1 - C_2, \\ &= (B_d - B_c)J(J+1). \end{aligned} \tag{8}$$

The combination defect is:[5]

$$\begin{aligned} [R(J) - Q(J)] - [Q(J+1) &- P(J+1)] \\ &= \Delta\nu_{dc}(J) + \Delta\nu_{dc}(J+1) \\ &\cong 2\Delta\nu_{dc}(J+\tfrac{1}{2}) \\ &\cong 2q(J+\tfrac{1}{2})(J+3/2) \\ &\cong 2q(J+1)^2. \end{aligned} \tag{9}$$

From the numerical values of the combination defect corresponding to the various quantum numbers J, the value of q was computed by least squares. It was found that $q = B_d - B_c = -6.7\times 10^{-5}$. In Fig. 1, the observed combination defects are plotted in comparison with a curve given by $-13.4\times 10^{-5}(J+1)^2$.

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[5] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

If the almost certainly correct assumption[5] is made that the $^1\Sigma$ lower electronic state of the observed bands is $^1\Sigma^+$, then the Q series lines originate from c levels.[4]

As mentioned before, there are a number of perturbations of the Q lines. This suggests the presence of other electronic energy levels near the $^1\Pi$ level. Since there are a number of perturbations of the Q lines, but not of the P and R lines, apparently the c levels are perturbed much more than the d levels and it seems likely that even for the unperturbed lines, it is the c levels rather than the d levels which are mainly responsible for the Λ-type splitting. If so (cf. Eqs. (7, 8)), $|C_2| \gg |C_1|$. Then since experimentally $(C_1 - C_2)$ is negative, C_2 would be positive. The expressions for the coefficients C_1 and C_2 are[5]

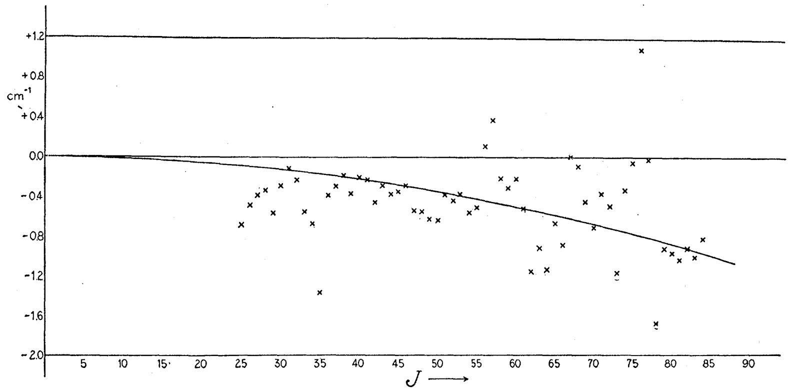

Fig. 1. The observed combination defects (cf. Eq. (9)) are shown by crosses. Each point indicated is, where possible, the average for the (0,1) (0,2), (0,3) and (0,4) bands. The curve is that given by $-13.4\times10^{-5}(J+1)^2$. Most of the small deviations between the experimental points and the curve may be due to experimental error, but most of the large ones are due to the perturbations of the Q lines.

$$\begin{aligned} C_1 &= 8\Sigma(\text{all } v \text{ values of all } {}^1\Sigma^+ \text{ states})\,|\,BL_y(\Pi, \Sigma^+)\,|\,^2/\nu(\Pi, \Sigma^+), \\ C_2 &= 8\Sigma(\text{all } v \text{ values of all } {}^1\Sigma^- \text{ states})\,|\,BL_y(\Pi, \Sigma^-)\,|\,^2/\nu(\Pi, \Sigma^-). \end{aligned} \tag{10}$$

The quantites BL_y are approximate constants for any pair of electronic states, Π, Σ. $\nu(\Pi, \Sigma^+)$ is the wave number (cm^{-1}) corresponding to the energy difference between the $^1\Pi$ state and v value considered and any $^1\Sigma^+$ state and v value. If the $^1\Pi$ level is above the $^1\Sigma^+$ level it is taken as positive, if it is below the $^1\Sigma^+$ level it is taken as negative. $\nu(\Pi, \Sigma^-)$ has a similar meaning. Hence, from the argument above, that $|C_2| \gg |C_1|$ and $C_2 > 0$, it would follow that $\nu(\Pi, \Sigma^-) > 0$. This would indicate the presence relatively close to and below the given $^1\Pi$ state of one or more $^1\Sigma^-$ levels, which cause perturbations of the c levels of the $^1\Pi$ state.

BAND ORIGINS

From the relation

$$\nu = \nu_0 + B_v'J'(J'+1) + D_v'J'^2(J'+1)^2 - B_v''J''(J''+1) - D_v''J''^2(J''+1)^2 \tag{11}$$

as the equation of a band line for a $^1\Pi \rightarrow {}^1\Sigma$ transition, the value of ν_0, for a given band, was taken as the definition of the band origin. With the observed wave numbers of twelve P, twelve R and ten Q lines of relatively small rotational quantum numbers, thirty-four values of ν_0 were calculated for the band under consideration. The average of these values was taken as the origin of the band. This was done for each of the five bands analyzed. Then a parabola was fitted by least squares to the values of ν_0 for the (0,1), (0,2), (0,3) and (0,4) bands, and by this means the values of ν_0 for the (0,0) and (0,5) bands were calculated. Then with aid of the values of B_v' and B_v'' the interval $(\nu_{\text{head}} - \nu_0)$ was calculated for most of the bands (other than those here analyzed) whose heads were measured by Jevons,[1] and with the wave numbers of the heads as listed by him, values of ν_0 were obtained. From the aggregate of the values of ν_0 calculations were made for ω_e', ω_e'', $x_e'\omega_e'$ and $x_e''\omega_e''$, giving greatest weight to the ν_0 data obtained directly by the present measurements, and the following equation was obtained for the origins of this band system:

$$\nu_0 = 42835.3 + 851.51(v'+\tfrac{1}{2}) - 6.143(v'+\tfrac{1}{2})^2 + 0.0437(v'+\tfrac{1}{2})^3 - 1242.03(v''+\tfrac{1}{2}) + 6.047(v''+\tfrac{1}{2})^2 - 0.00329(v''+\tfrac{1}{2})^3. \tag{12}$$

MOLECULAR CONSTANTS

In Table III there are listed the values of all the molecular constants obtained in the present work. The values of β' and β'' corresponding to the relation

$$D_v = D_e + \beta(v+\tfrac{1}{2}) = D_0 + \beta v \tag{13}$$

were calculated from the theoretical formula[6]

$$\beta = \frac{\alpha^2}{6\omega_e} + \frac{20\alpha B_e^2 - 32x_eB_e^3}{\omega_e^2}\,. \tag{14}$$

A check on the correctness of the analysis was afforded by a rule, due to R. T. Birge. According to this rule the quantity $2x_eB_e/\alpha_e$ is approximately equal to 1.4. For these bands substitution of the proper values showed that

$$2x_e'B_e'/\alpha' = 1.38$$
$$2x_e''B_e''/\alpha'' = 1.43.$$

An additional check is given by the approximate relation[7] that for molecules composed of two atoms of nearly equal mass, the quantity $r_e^3\omega_e$ is approximately equal to 3000×10^{-24} cm². For these bands

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[6] E. C. Kemble, Jour. Opt. Soc. Am. **12,** 1 (1926).

[7] P. M. Morse, Phys. Rev. **34,** 57 (1929).

$$r_e'^3\omega_e' = 3620 \times 10^{-24}$$
$$r_e''^3\omega_e'' = 4276 \times 10^{-24}.$$

TABLE III. *Values of the molecular constants.*

Upper state $^1\Pi$	Lower state $^1\Sigma$
$B_e'=0.6303$	$B_e''=0.7263$
$B_0'=0.6270$	$B_0''=0.7238$
$B_1'=0.6205$	$B_1''=0.7189$
$\alpha'=0.00657$	$B_2''=0.7138$
$D_e'=-1.382\times10^{-6}$(calc.)	$B_3''=0.7091$
$\beta'=2.88\times10^{-9}$ (calc.)	$B_4''=0.7041$
$I_e'=43.95\times10^{-40}$ g cm^2	$\alpha''=0.00494$
r_e' (for $Si_{28}O_{16}$) $=1.62\times10^{-8}$ cm	$D_e''=-0.993\times10^{-6}$ (calc.)
$q=B_d-B_c=-6.7\times10^{-5}$	$\beta''=-1.55\times10^{-9}$ (calc.)
$\omega_e'=851.5$	$I_e''=38.14\times10^{-40}$ g cm^2
$x_e'\omega_e'=6.14$	r_e''(for $Si_{28}O_{16}$) $=1.51\times10^{-8}$ cm
$y_e'\omega_e'=0.0437$	$\omega_e''=1242.0$
	$x_e''\omega_e''=6.05$
	$y_e''\omega_e''=0.00329$

It is to be expected that for SiO the values of $r_e'^3\omega_e'$ and $r_e''^3\omega_e''$ will be greater than 3000×10^{-24}, since the masses of the two atoms are rather unequal.

The writer wishes to express his thanks to Professor R. S. Mulliken for proposing this problem and for his valuable advice and suggestions; also to Professor W. F. C. Ferguson of New York University for the spectrograms taken by him with the large quartz spectrograph, and to Dr. W. F. Meggers of the Bureau of Standards for the use of the latter.