the two minima in the solution spectrum at 2.65 and 2.80μ should be identified with the centers of the σ and π bands, the latter occurring through a breakdown of selection rules in the solution, cannot be settled at present. A significant fact is the agreement of the position of the shoulder in the liquid curve with the center of the solution doublet. It suggests that the minimum in the liquid on the long wave-length side of the solution band is caused by polymer or lattice couplings and that in the liquid free molecules still exist in sufficient numbers to produce their own type of absorption without appreciable shift with respect to their absorption in solution.

The question of the existence of line structure in the solution spectrum also cannot be answered with the present resolving power. The fact that some structure which appears in the vapor in the 1.875μ band seems to be absent in the solution spectrum makes it likely that line structure is wiped out by the broadening of the vibrational centers caused by the perturbing effects of the carbon disulfide molecules. Broadening of the order of 10–20 cm^{-1}, the distance between individual lines, would be sufficient to wipe out such structure.

The structure which the bands of the solution spectrum show indicates that regardless of which of the two suggested correlations turns out to be the correct one rotation of the molecules in the solution occurs. The occurrence of free rotation under these conditions can be predicted on the basis of the work of Debye. Debye[3] has calculated that in liquid water a molecule must possess an energy of 10 kT before it can rotate 90° in the field of its neighbors. If his method is applied to the water molecule in benzene, the case for which its electric moment is known, the energy E that it must possess before it can turn through 90° is approximately kT. This follows from Debye's equations, $y=E/kT$, and $R(y)=1-L^2(y)$, where $L(y)$ is Langevin's function, and $R(y)$ is the ratio of the molar polarization of the molecule in solution (64 cm^3) to that of the free molecule (71 cm^3). Since the dipole behavior of water in carbon disulfide seems likely to differ little from its behavior in benzene, this criterion shows that free rotation will very probably occur.

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The Structure of the α and β Band Systems of SiF

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A new vibrational analysis of the α system of SiF is presented. The rotational structure of the (0, 0) band of this system is analyzed, giving $B_0''=0.5795$ and $B_0'=0.5743$, and confirming the nature of the transition to be $^2\Pi_{\text{reg.}}\rightarrow{}^2\Pi_{\text{reg.}}$, with the upper state extremely near to case b and the lower state near case a. The doublet separation in the lower state is determined, but the spin doubling in the upper state is found too small to be accurately evaluated. The Λ type doubling is discussed. The rotational structure of the (0, 0) band of the β system is also analyzed, and the transition confirmed to be of the type $^2\Sigma\rightarrow{}^2\Pi_{\text{reg.}}$, the $^2\Pi$ state being the lower state in the α system. For the $^2\Sigma$ state $B_0=0.622$ is obtained, being less accurate than the values for the other two states because of experimental difficulties encountered in photographing this band. The spin doubling in the $^2\Sigma$ state is discussed, and the constants of the known electronic states of SiF are summarized.

INTRODUCTION

The spectrum of a discharge through silicon tetrafluoride gas was carefully photographed several years ago by Johnson and Jenkins,[1] who discovered a large number of strong bands in the region between 2100 and 7000A, in addition to the blue system observed by Porlezza[2] in 1911. They were able to divide this entire spectrum into five band systems, to which they assigned the designations α, β, γ, δ, and ϵ. Vibrational

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[1] Johnson and Jenkins, Proc. Roy. Soc. **A116**, 327 (1927).

[2] Porlezza, Rend. Acad. Linc. **20**, 488 (1911); also **33**, 283 (1924).

analyses of the α and β systems were proposed, and a rotational analysis of the strong band at 4368A, called the (0, 0) band of the former, attempted. Their results led them, however, to rather improbable conclusions concerning the emitter of the spectrum. It was subsequently shown in this laboratory, by Badger and Blair,[3] that the band at 4368A was of a more complex nature than had been supposed from the apparently simple structure at its origin. A new interpretation of the original band head data was recently given by Asundi and Samuel,[4] who proposed vibrational analyses for the α, β, and γ systems, attributing the first to a $^2\Pi \rightarrow {}^2\Pi$, and each of the latter to a $^2\Sigma \rightarrow {}^2\Pi$ transition. While their analyses of the β and γ systems are satisfactory, that of the α system not only appears incompatible with the observed band intensities, but also gives as the ratio A/B for the upper state, which must be very near to case b because of the strong satellite branches, the value 48, which is certainly many times too large.

In the following report is presented a new interpretation of these data which removes the two above objections, and also rotational analyses of the (0, 0) bands of both the α and β systems.

EXPERIMENTAL

For all of the photographs employed in this investigation, the spectrum was excited by a discharge through silicon tetrafluoride gas, in essentially the manner described by Johnson and Jenkins. The excellent set of high dispersion plates of the α system obtained in this laboratory by Dr. C. M. Blair, who has kindly placed them at my disposal, were taken in the third order of a 21-foot concave grating, where the dispersion was 0.78 A/mm. The bands appeared with such great intensity that a small air-cooled Pyrex discharge tube with aluminum electrodes provided an adequate source. Exposures were of the order of one to two hours. The lines were relatively sharp, and all could be easily measured directly under the comparator with respect to standard iron lines in the third order.

The β system was photographed by the author in the fourth order of the same grating, obtaining a dispersion of 0.58 A/mm. A filter consisting of a saturated solution of very pure nickel sulfate was found effective in separating this order from the third, which contained some of the bands of the much stronger α system. A 5 mm layer completely removed the region of the spectrum between 3600 and 4300A, but was very transparent in the ultraviolet. The low intensity of the β system, the high dispersion, and the poor reflecting power of the grating in this region of the spectrum made adequate exposures difficult to obtain. A large Pyrex discharge tube with a quartz window and massive aluminum electrodes was used. It was completely water cooled, and run on the secondary of a 5 kva General Electric transformer. The silicon tetrafluoride was pumped continuously through the tube at about 1 mm pressure, and the voltage in the primary adjusted to give maximum intensity. The most satisfactory plates were exposed for fifty hours, but even then much of the structure was difficult or impossible to measure directly under the comparator. Consequently most of the lines were measured on enlarged microphotometer curves, using as references the strong lines of the Q branches, which were directly measurable on the plates with respect to iron lines in the third order. Test measurements of a number of standard iron lines photographed in the second and third orders have disclosed no systematic error arising from the use of the method of coincidences with this grating.

THE STRUCTURE OF THE α SYSTEM

Vibrational analysis

Careful consideration of the high dispersion plates of the α system reveals that all strong heads may be grouped in pairs of approximately equal intensity, separated by an interval very nearly equal to the doublet separation in the β system. Each strong head is, in addition, accompanied by an apparently weaker head on the high frequency side, so that a complete band consists of four heads. The strongest of these bands, which includes the head at 4368A, appears to be the (0, 0) band of the system. The principal sequence can be traced to the (8, 8) band, and the first four bands of the (1, 0) sequence are clearly visible, though many times weaker than the

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[3] Badger and Blair, Phys. Rev. **47**, 881 (1935).

[4] Asundi and Samuel, Proc. Ind. Acad. Sci. **3**, 346 (1936).

former. The (0, 1) and (5, 5) bands are both rather weak and seem to be in almost perfect coincidence, but some of the higher members of the (0, 1) sequence are observed, separated from the overlapping bands of the principal sequence. A few bands of the (0, 2) sequence are also present, but too weak to have been accurately measured. This analysis of the data of Johnson and Jenkins is presented in Table I.

Comparison of the $\Delta G''(v)$ values obtained from the strong heads with those obtained by Asundi and Samuel from the Q heads of the β system shows satisfactory agreement, and indicates that these two systems do indeed possess a common lower state. Since band heads, instead of origins, have been used, differences are to be expected, but these should decrease for higher values of v, since the heads appear to draw in toward the origins in ascending each sequence, approaching rather rapidly some nearly constant separation. Such is seen to be the case. From the $\Delta G'(v)$ values the vibrational constants of the upper state may be determined, and when most weight is given those differences for which v is

TABLE I. *Vibrational analysis of the α system of SiF.*

v' \ v''	0	1	2	3	4	5	6	7	8	
0	22958.4 22886.2 22780.1 22718.3	— 22040.1 — 21878.2	— — — 21037							687.7
1	23613 23573.9 23448.4 23411.6	22789.4 22729.9 22613.4 22565.9	— 21900 — —	— — — 20911						676.5
2		23440.1 23404.3 23772.4 23242.4	22610.7 22568.1 22442.8 22405.4	— — — 21577	— 20930 — 20761					659.0
3			23256.1 23226.7 23090.1 23065.0	22434.2 22399.1 22267.4 22236.9	21622 21577 21456 21413	— 20733 — 20611				642
4				23066.3 23041.7 22901.3 —	22252.8 22222.9 22086.4 22061.0	— 21413 — 21252	— 20611 — 20448			627
5						— 22040.1 — 21878.2	— — — —	— — — 20421		
6							— 21851.5 — 21689	— — — —	— — — 20112	
7								— 21655 — 21497	— — — —	
8									— 21456 — —	↑
	845.3 847.3	836.0 838.2	827.9 828.0	817.4 817.7	809.5 811.5	803 (α system) 800.8 (β system)	←	Means of first differences		

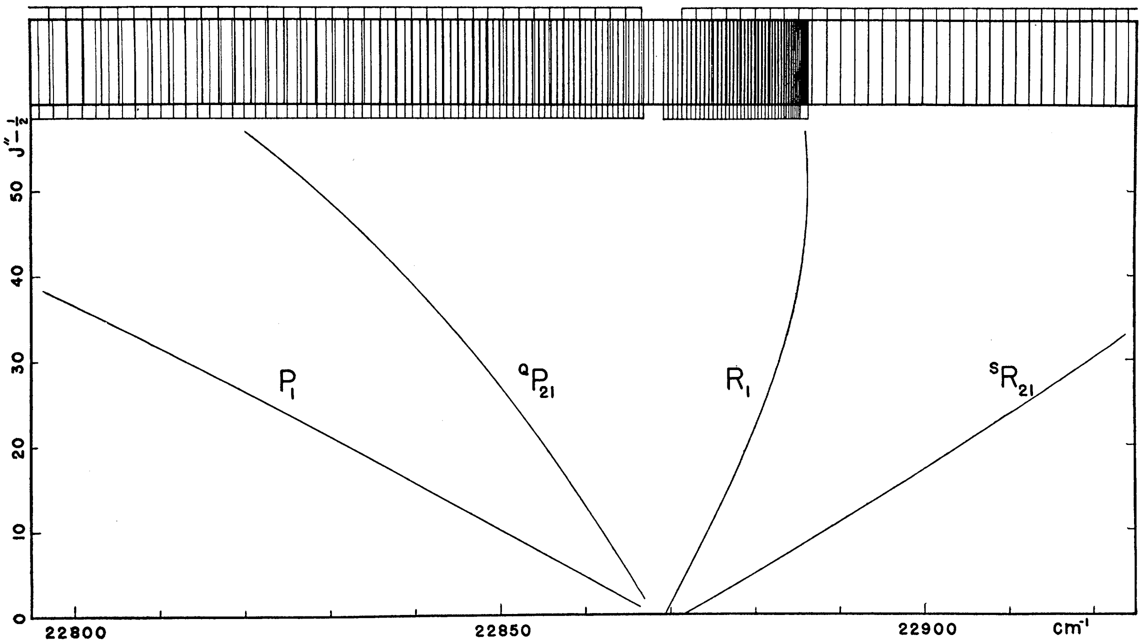

FIG. 1. The lines, disposition of branches, and Fortrat diagram of the high frequency sub-band of the (0, 0) band of the α system. The two unmarked lines near the origin are the first two lines of the weak Q_1 branch.

large, the results should be rather reliable. The best values obtained by this method are:

$$\omega_e = 710.9 \text{ cm}^{-1}, \qquad x_e\omega_e = 8.6 \text{ cm}^{-1}.$$

These results at once imply certain conclusions concerning the electronic states involved in the α system. Since the lower state seems certainly to be $^2\Pi$, the absence of strong Q branches at the origin of the (0, 0) band means that the upper state must also be $^2\Pi$. But the approximate equality of the doublet separations in the α and β systems suggests that this $^2\Pi$ state is very near to case b, under which circumstances branches violating the Σ selection rule, as observed in the ultraviolet spectrum of O_2^+ by Stevens,[5] are to be expected. Each band would then include four head forming branches, as observed in the α system. Since $\omega_e'' - \omega_e'$ is nearly equal to the doublet separation in the lower $^2\Pi$ state, overlapping of bands is so complete that the rotational analysis has been of necessity limited to the (0, 0) band.

Rotational analysis

The analysis of the (0,0) band of the α system, whose four heads occur at 4354, 4368, 4388, and 4400A, was begun on the assumption that it arose from a transition between states of the type described above. In the most general case, such a band is divided into two twelve-branch sub-bands, separated by a frequency equal approximately to the magnetic coupling constant, A''. The high frequency sub-band includes the $^SR_{21}$, R_1, $^RQ_{21}$, Q_1, $^QP_{21}$, and P_1 branches, and the low frequency component the R_2, $^QR_{12}$, Q_2, $^PQ_{12}$, P_2, and $^OP_{12}$ branches, each of which is itself a double branch because of the Λ type doubling of the rotational levels. Actually, however, the latter is small, and the resulting four Q branches are not only weak, but also coalesce with their P and R branch neighbors when the spin doubling in the upper state is small, which proves to be the case in this system. Hence each sub-band consists essentially of four branches, whose arrangement is shown in Fig. 1 for the high frequency component of the (0, 0) band. The appearance of the other sub-band is very similar to that shown, with the positions of regular and satellite branches interchanged.

The lines of the $^SR_{21}$ and R_2 branches, which occupy analogous positions in the two sub-bands, were completely free from overlapping beyond

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[5] Stevens, Phys. Rev. **32**, 1292 (1931).

their first ten lines, which were hence easily located by extrapolation. The R_1 and ${}^QR_{12}$ branches were observable from their first lines to their heads, but in neither case could the returning branch be detected. The ${}^QP_{21}$ and P_2 branches were followed from their first lines to beyond $J=60\frac{1}{2}$, but the P_1 and ${}^OP_{12}$ branches, whose spacings are about twice those of the former, coincided with them at around $J=19\frac{1}{2}$, and were impossible to follow below $J=15\frac{1}{2}$. In the high frequency sub-band, these coincidences were so good that the P_{21} and R_1 branches were mistaken by Johnson and Jenkins for the P and R branches of a simple $\Sigma\rightarrow\Sigma$ band. Since the first lines of the

TABLE II. *The (0, 0) band of the α system of SiF.*

$J-\frac{1}{2}$	${}^SR_{21}$	R_1	${}^QP_{21}$	P_1	R_2	${}^QR_{12}$	P_2	${}^OP_{12}$
0	22871.33	22869.24						
1	73.08	69.77		22866.64	22712.38	22709.13		22705.96
2	74.82	70.36	22866.89	64.80	14.07	09.64	22706.32	04.09
3	76.55	70.89	66.30	62.97	15.75	10.14	05.48	02.22
4	78.27	71.44	65.70	61.15	17.41	10.63	04.77	00.36
5	79.98	71.97	65.11	59.33	19.05	11.11	04.13	698.47
6	81.68	72.49	64.50	57.57	20.68	11.57	03.46	96.65
7	83.37	72.99	63.88	55.77	22.30	12.02	02.82	94.80
8	85.05	73.54	63.25	54.06	23.90	12.48	02.10	93.00
9	86.70	74.05	62.62	52.25	25.48	12.97	01.38	91.16
10	88.40	74.57	62.00	50.47	27.05	13.33	00.64	89.23
11	90.05	75.04	61.33	48.63	28.60	13.73	699.94	87.32
12	91.70	75.55	60.70	46.89	30.13	14.13	99.17	85.47
13	93.30	76.02	60.03	45.06	31.65	14.54	98.39	83.58
14	94.95	76.50	59.38	43.24	33.13	14.91	97.58	81.65
15	96.54	76.97	58.69	41.39	34.63	15.25	96.78	79.67
16	98.16	77.43	58.03	39.58	36.09	15.55	95.95	77.70
17	99.76	77.91	57.35	37.77	37.54	15.82	95.10	75.68
18	901.32	78.34	56.65	35.90	38.96	16.13	94.24	73.69
19	02.89	78.77	55.93	34.01	40.35	16.40	93.37	71.66
20	04.49	79.21	55.22	32.19	41.77	16.67	92.49	69.66
21	06.05	79.59	54.53	30.34	43.15	16.94	91.63	67.60
22	07.59	80.02	53.80	28.38	44.51	17.13	90.70	65.55
23	09.12	80.43	53.06	26.59	45.87	17.38	89.76	63.44
24	10.66	80.80	52.29	24.66	47.17	17.57	88.80	61.40
25	12.19	81.18	51.54	22.78	48.48		87.81	59.27
26	13.68	81.61	50.77	20.86	49.75		86.83	57.10
27	15.17	81.96	49.97	18.94	51.01		85.86	54.96
28	16.65	82.33	49.18	17.02	52.27		84.84	52.83
29	18.12	82.69	48.39	15.10	53.49		83.80	50.63
30	19.59	83.03	47.57	13.07	54.68		82.73	48.47
31	21.02	83.33	46.77	11.18	55.88		81.63	46.25
32	22.43	83.65	45.93	09.22	57.06		80.54	44.03
33	23.86	83.91	45.09	07.25	58.17	head	79.44	41.76
34	25.25	84.18	44.22	05.25	59.27	18.38	78.31	39.48
35	26.64	84.39	43.34	03.26	60.38		77.15	37.21
36	28.00	84.62	42.47	01.11	61.43		75.96	34.93
37	29.35	84.90	41.60	799.18	62.47		74.76	32.57
38	30.69	85.06	40.68	97.16	63.49		73.52	30.21
39	31.97	85.27	39.75	95.11	64.50		72.30	27.86
40	33.31		38.82	93.05	65.44		71.06	25.49
41	34.54		37.86	90.98	66.41		69.75	23.11
42	35.81		36.87	88.87	67.34		68.45	20.63
43	37.13		35.91	86.78	68.18		67.12	18.18
44	38.30		34.91	84.63	69.10		65.81	15.70
45	39.47		33.85	82.51	69.91		64.40	13.27
46	40.66	head	32.82	80.36	70.74		62.97	10.74
47	41.78	86.22	31.79	78.15	71.51		61.54	08.11
48	42.97		30.70	76.02	72.32		60.09	05.33
49	44.05		29.63	73.83	72.97		58.63	
50	45.12		28.51	71.55	73.65		57.15	
51	46.15		27.33	69.34	74.35		55.58	
52	47.23		26.21	67.08	74.96		53.99	
53	48.22		25.00	64.76	75.59		52.42	
54	49.17		23.77	62.29	76.19		50.81	

Also the lines $Q_1(\frac{1}{2})=22867.47$ and $Q_1(1\frac{1}{2})=22868.04$. ${}^PQ_{12}(1\frac{1}{2})$ was too confused to be measured.

R_1, $^QR_{12}$, $^QP_{21}$, and P_2 branches were visible, their numberings were determined at once. The first lines, and hence the numberings, of the extrapolated $^SR_{21}$ and R_2 branches were then chosen to provide the correct number of missing lines. The numbering and the frequency of the lower lines of the two remaining branches were determined by means of the term differences in the upper state. The $^RQ_{21}$ and Q_1 branches were found to have coalesced with the R_1 and $^QP_{21}$ branches, but since the Q_1 branch begins with $J=\frac{1}{2}$ and the $^QP_{21}$ with $J=2\frac{1}{2}$, the first two lines of the former were observed, and proved to be of the expected low intensity. In the other sub-band an analogous situation occurs, the first line of the $^PQ_{12}$ branch being observable, since it begins with $J=1\frac{1}{2}$, while the P_2 branch begins with $J=2\frac{1}{2}$. All of the lines below $J=55\frac{1}{2}$ are listed in Table II, the measurements being made in all cases to the center of the Λ doublets.

The rotational terms of the upper and lower states may be expressed by the following equations, which follow immediately from the application to the $^2\Pi$ state of the general expressions for case *a* and case *b* molecular multiplets,[6] assuming the Λ doubling negligible in the upper state, and including all functions independent of J, K, and Σ as the quantity T_0, which will hence be constant for any one band:

$$\begin{aligned}
T_1'(K)&=T_0'+f(K,+\tfrac{1}{2})+B_v'K(K+1)\\
&\qquad+D_v'K^2(K+1)^2+\cdots,\\
T_2'(K)&=T_0'+f(K,-\tfrac{1}{2})+B_v'K(K+1)\\
&\qquad+D_v'K^2(K+1)^2+\cdots,\\
T_1''(J)&=T_0''-A''/2-B_{v1}''^*/4+\phi_i(-\tfrac{1}{2},J)\\
&\qquad+B_{v1}''^*J(J+1)+D_{v1}''^*J^2(J+1)^2+\cdots,\\
T_2''(J)&=T_0''+A''/2-9B_{v2}''^*/4+\phi_i(+\tfrac{1}{2},J)\\
&\qquad+B_{v2}''^*J(J+1)+D_{v2}''^*J^2(J+1)^2+\cdots.
\end{aligned}\tag{1}$$

The constants of the lower state marked with asterisks are introduced to allow for a tendency toward case *b*. They are given, according to the theory of Hill and Van Vleck,[6] by the following expression, for a $^2\Pi$ state:

$$B_v^*=B_v(1\pm B_v/A).\tag{2}$$

The value of B_{v2}^* is given by the upper, and of B_{v1}^* by the lower sign.

Aside from the Λ doubling, the term differences are given by the relations:

$$\begin{aligned}
\Delta_2T_1'(J)&=R_1(J)-P_1(J)\\
&={}^QR_{12}(J)-{}^OP_{12}(J),\\
\Delta_2T_2'(J)&=R_2(J)-P_2(J)\\
&={}^SR_{21}(J)-{}^QP_{21}(J),\\
\Delta_2T_1''(J)&=R_1(J-1)-P_1(J+1)\\
&={}^SR_{21}(J-1)-{}^QP_{21}(J+1),\\
\Delta_2T_2''(J)&=R_2(J-1)-P_2(J+1)\\
&={}^QR_{12}(J-1)-{}^OP_{12}(J+1).
\end{aligned}\tag{3}$$

Eqs. (1) show that, if the small quantities $\Delta_2f(K,J-K)$ be neglected:

$$\begin{aligned}
\Delta_2T_1'/2(2K+1)&=\Delta_2T_2'/2(2K+1)\\
&=B_v'+2D_v'(K^2+K+1)+\cdots.
\end{aligned}\tag{4}$$

Hence when the left side of (4) is plotted against $(K+\frac{1}{2})^2$, a straight line of slope $2D_v'$ and intercept $B_v'+\frac{3}{2}D_v'$ should be obtained. Such a graphical treatment of the term differences obtained from the $^SR_{21}$, $^QP_{21}$, R_2, and P_2 branches enabled B_0' to be evaluated within an uncertainty of ± 0.0001 cm^{-1}, and D_0' within limits of about ± 1.5 percent. Exactly analogous expressions in terms of J apply to the lower state, and the constants were found in the same manner, with comparable results. The values so determined are as follows:

$$\begin{aligned}
B_0''&=0.5795\text{ cm}^{-1}, & D_0''&=-1.12\times10^{-6}\text{ cm}^{-1},\\
B_0'&=0.5743\text{ cm}^{-1}, & D_0'&=-1.59\times10^{-6}\text{ cm}^{-1}.
\end{aligned}$$

The value of A'' was determined by the following relation, obtained from Eqs. (1) by neglecting the term $\phi_i(\Sigma, J)$:

$$\begin{aligned}
A''+(B_{01}''^*-9B_{02}''^*)/4&={}^QP_{21}(J)\\
&\quad-P_2(J)-J(J+1)(B_{02}''^*-B_{01}''^*)+\cdots.
\end{aligned}\tag{5}$$

The right-hand expression was found to be constant within the experimental error, when evaluated for the first twelve lines of the two branches, and gave the average value of 160.83 cm^{-1}. Hence, with Eq. (5), the value of A'' may be obtained, and is found to be $+161.99$ cm^{-1}, making A''/B_0'' equal to $+279.53$. The latter indicates that the lower $^2\Pi$ state is, as was assumed, intermediate between case *a* and case *b*, but much closer to the former.

The intensity of the satellites, the doublet separation in the α system, and the coalescence of branches already remarked indicate that the

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[6] Mulliken, Rev. Mod. Phys. **2**, 105, 114 (1930).

upper $^2\Pi$ state is very near to case *b*. It would hence be anticipated[7] that the spin doublet separation be given by the expression:

$$\Delta f(K)=[A'/K(K+1)+\gamma_i](K+\tfrac{1}{2}), \qquad (6)$$

where the value of γ_i is different for the *c* and *d* sub-levels.[8] Since γ_i is almost negligibly small in this case, and since, moreover, the Λ doublets are unresolved at low values of J, it may be replaced by an average value $\gamma_{\text{av.}}$, in the calculation of A'. With this assumption, Eq. (6), combined with Eqs. (1), gives the expression:

$$[{}^QR_{12}(J)-P_2(J+1)]/(J+1)-2B_{02}''^* \\ -4J^2D_{02}''^*=A'/(J+\tfrac{1}{2})(J+\tfrac{3}{2})+\gamma_{\text{av.}} \qquad (7)$$

An analogous equation applies in the other sub-band. The left-hand expression in (7) plotted against $1/(J+\frac{1}{2})(J+\frac{3}{2})$ should give a straight line of slope A' and intercept $\gamma_{\text{av.}}$. When actually attempted, it was found that these quantities were of the order of magnitude of the experimental errors, so that no unique line was determined. It can only be stated that A' is surely positive, and probably less than 0.10 cm^{-1}. This means that A'/B_0' is about 0.17, and that the upper state is as close to case *b* as the $^2\Pi$ state of BeH.[9]

The origins of the two sub-bands cannot be precisely determined without exact values of A' and γ_i, but the following values, obtained from the R_1 and P_2 branches are probably quite accurate:

$$\nu_{01}=T_0'-T_0''+A''/2+B_{01}''^*/4=22868.50\text{ cm}^{-1},$$
$$\nu_{02}=T_0'-T_0''-A''/2+9B_{02}''^*/4 \\ =22707.70\text{ cm}^{-1}.$$

The P_2 and ${}^QP_{21}$ branches can be followed out to very high values of J, where the Λ doublets are well resolved. Between $J=35\frac{1}{2}$ and $70\frac{1}{2}$, the doubling in the $^2\Pi_{\frac{1}{2}}$ state is well represented by the expected relation:[10]

$$\phi_c(J)-\phi_d(J)=a(J+1/2). \qquad (8)$$

The constant a is found to be 0.0067 cm^{-1}. The doubling in the $^2\Pi_{1\frac{1}{2}}$ state is less accurately observable because of the overlapping (1, 1) band, but beyond $J=40\frac{1}{2}$ it is of about the same order of magnitude, but increasing more rapidly and nonlinearly with $J+1/2$. This behavior of the Λ doublets indicates that they arise almost entirely from doubling of the rotational levels of the case *a* $^2\Pi$ state.

The Structure of the β System

Vibrational structure

Asundi and Samuel's analysis of the band head data attributes the β system to a $^2\Sigma\rightarrow{}^2\Pi$ transition, but the constants of Johnson and Jenkins have been but slightly altered, since the doublet separation was found to be very nearly equal to $\omega_e'-\omega_e''$. The resulting superposition is remarkably accurate in the bands near the origin of the system, measurable separations commencing only in the weaker (2, 0), (0, 2), and (0, 3) sequences, where the extra heads were supposed by Johnson and Jenkins to arise from a vibrational isotope effect. Of course the isotopic displacement coefficient failed to agree with any calculated from masses of silicon isotopes. Careful investigation of heavily exposed photographs of this system taken on a quartz Littrow spectrograph giving a dispersion of 3.7A/mm in the vicinity of 2900A showed no evidence of true isotopic heads.

Because of the coincidence remarked above, only the low frequency sub-band of the first band of each sequence would be expected to be free from complete overlapping. Fortunately, however, the Franck-Condon diagram for the system is a narrow parabola, the only member of the principal sequence appearing with appreciable intensity being the (0, 0) band itself. Beside being confused by this superposition, the (0, 1) and (1, 0) bands were too weak after 50 hours exposure to permit analysis, which consequently was limited to the (0, 0) band.

Rotational analysis

The (0, 0) band, whose heads occur at 2880, 2881, 2893, and 2894A, would be expected to consist of six regular and two satellite branches, if the spin doubling in the $^2\Sigma$ state were small. Such is found to be the case, though measurable spin doublets are observed in the higher members of the Q_1 branch. Of the six regular branches, three are head forming, while the fourth head of the complete band is formed by one of the satellites. All six main branches are observed, but only the head forming ${}^OP_{12}$ satellite is found, and its individual lines, despite their favorable

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[7] Mulliken and Christy, Phys. Rev. **38**, 87 (1931).

[8] Mulliken, Rev. Mod. Phys. **2**, 108, 110 (1930).

[9] Watson and Parker, Phys. Rev. **37**, 167 (1931).

[10] Mulliken, Rev. Mod. Phys. **3**, 113 (1931).

location, were not measurable. The ${}^SR_{21}$ branch is presumably hidden by the stronger regular branches. The observed intensity relations among these branches confirm Asundi and Samuel's conclusion that the β system arises from a ${}^2\Sigma\rightarrow{}^2\Pi$ transition.

Because of the low total intensity, of which, moreover, less than half is divided among the P and R branches, the latter were hidden at low values of J by the strong Q branches, while all of the branches of the low frequency sub-band were lost when they overlapped the P_1 head of the second sub-band. The latter branch, moreover, could not be followed through the strong Q_1 head. It was therefore necessary to number the lines in an indirect manner. Only one method of numbering gave both the same term differences in the upper state, given by Eqs. (3), and also a reasonable value of D_0'. The term differences in the lower state were then found in agreement with those obtained from the α system. The Q branches were numbered by the approximate relation

$$R(J)-Q(J)=Q(J+1)-P(J-1). \qquad (9)$$

TABLE III. *The (0, 0) band of the β system of SiF.*

$J-\frac{1}{2}$	P_1	Q_1	R_1	${}^OP_{12}$	P_2	Q_2	R_2
0							
1						34559.91	
2	head	head		head	head	60.78	
3	34702.43	34717.39		34559.98	34556.47	61.76	
4						62.76	
5						63.81	
6						64.99	
7						66.22	
8		18.04				67.54	
9		18.47				69.61	
10		18.94				70.51	
11		19.54				72.18	
12		20.23				73.85	
13		——				75.69	
14		——				77.62	
15		——	34740.86			79.63	
16		22.85	43.15		61.16	81.63	
17		23.83	45.65		62.15	83.79	
18		24.97	48.12		63.04	85.98	
19		26.26	50.61		64.10	88.32	
20		27.57	53.18		65.41	90.83	34618.71
21		29.05	55.88		66.62	93.39	22.51
22		30.60	58.71		68.04	95.98	26.37
23		32.23	61.22		69.41	98.60	30.46
24	03.35	33.94	64.07		70.93	601.37	34.46
25	03.92	35.82	67.24		72.68	04.28	38.41
26	04.52	37.70	70.17		74.34	07.31	42.54
27	05.18	39.71	73.32		76.04	10.33	46.78
28	05.96	41.84	76.68		77.90	13.71	51.10
29	06.90	44.11	80.04		79.94	17.56	55.49
30	07.82	46.38	83.54		82.09	20.14	60.11
31	08.84	48.76	86.95		84.16	23.57	64.80
32	09.97	51.18	90.50		86.40	27.10	69.53
33	11.16	53.95	94.10		88.83	30.67	74.56
34	12.63	56.56	98.13		91.17	34.30	79.12
35	14.17	59.39	802.00		93.76	38.09	
36	15.78	62.24	05.78		96.36	41.93	
37		65.16	09.80		98.99	45.87	
38		68.33	14.09		601.77	49.86	
39		71.50	18.36		04.63	53.96	
40		74.88	22.68		07.65	58.07	
41		78.04	27.23		11.04	62.46	
42		81.39	32.31		14.26	66.78	
43		85.02	37.03		17.51	70.07	
44		88.57	41.95		20.72	75.75	
45		92.36	47.06		24.34		
46		96.11	52.12				
47		800.12	57.25				
48		04.21	62.45				
49		08.25	67.42				
50		12.47	72.77				

TABLE IV. *Constants of the SiF molecule.*

STATE	$T_e+G(0)$ (cm^{-1})	$T_e+G(0)$ (volts)	ω_e (cm^{-1})	$x_e\omega_e$ (cm^{-1})	B_0 (cm^{-1})	r_0 (A)
$C^2\Sigma$	39531.5[1]	4.877[1]	891.7[1]	6.2[1]		
$B^2\Sigma$	34717.39	4.283	1011.2[1]	4.8[1]	0.662	1.54
$A^2\Pi_{\text{reg.}}$	22868.50	2.821	710.9	8.6	0.5743	1.606
$X^2\Pi_{\text{reg.}}$	160.83 0	0.020 0	856.7[1]	4.7[1]	0.5795	1.599

[1] Asundi and Samuel, Proc. Ind. Acad. Sci. **3**, 346 (1936).

An independent numbering was also possible, since when the first differences are plotted against J, they extrapolate to $-B_{01}''^*$ at $J=-1/2$, for the Q_1, and to $+B_{02}''^*$ at $J=-3/2$, for the Q_2 branch. The two numberings were found identical, though it seems impossible to obtain the Λ doubling in the $^2\Pi$ state by the usual combinations with the Q branches. This is probably to be expected from the small magnitude of the doubling, and the extreme difficulties and certain errors involved in the measurements of the lines. The frequencies and numbering of the lines are shown in Table III.

B_0' was determined by the graphical method already described, but since so few combinations were available, the slope of the line was determined independently by Kratzer's relation

$$D_e=-4B_e^3/\omega_e^2. \tag{10}$$

From the slope so obtained, B_0' was found to be equal to 0.622 cm^{-1}.

From the separations of the Q_1 and $^RP_{21}$ branches, which are measurable beyond $J=50\frac{1}{2}$, the value of the spin doubling coefficient γ was found to be approximately 0.011 cm^{-1}.

CONCLUSION

It is felt that the present analysis establishes with reasonable certainty the nature of three of the electronic states of the SiF molecule, while Asundi and Samuel's vibrational analysis of the γ system suggests the nature of a fourth state to be $^2\Sigma$, though it could scarcely be distinguished with certainty from a close $^2\Delta$ without further investigation. The known constants of these four states are collected in Table IV, where the upper state of the γ system is designated $C^2\Sigma$, in accordance with the conclusions of Asundi and Samuel.

The $A^2\Pi$ state of this molecule has proved to be a most unusual and interesting one. The occurrence of nearly pure case b coupling in the $^2\Pi$ state of so heavy a molecule is itself unique, and the (0, 0) band of the α system, with its visible origin and strong satellite branches, provides an excellent example of the rotational structure of a $^2\Pi$ (case b)$\rightarrow$$^2\Pi$ (case a) band. In addition, this state appears to constitute a genuine exception to such empirical relations as Badger's rule[11] between r_e and ω_e, for while r_e is very nearly the same in the two states, ω_e differs by 145.8 cm^{-1}. Of course, such empirical rules mean only that a fairly consistent relationship has been found to exist between the position of the minimum in the potential functions of ordinary molecules and the value of the second derivative at that point, while their failure in any particular case signifies a deviation of its potential function from the usual type. The $^1\Pi$ state of AlH, for example, is obviously unusual in possessing a dissociation energy of only 0.26 ev, and ω_e is observed to be about 600 cm^{-1} lower than calculated from r_e. Though the extreme case b coupling in the $A^2\Pi$ state of SiF is extraordinary, there exists no obvious correlation between it and the low value of ω_e, for the latter shows no trend away from the normal in the $^2\Pi_u$ state of O_2^+, which approaches case b, nor in the nearly pure case $b^2\Pi$ states of CH or BeH. Since there exist no extended vibrational progressions in the α system, little can be definitely stated concerning the magnitude of the dissociation energy for the $A^2\Pi$ state, and the nature of the potential function at points far from the equilibrium position. It does, however, appear that the two $^2\Pi$ states are derived from the same electronic states of the silicon and fluorine atoms, and should be analogous to the $^2\Pi$ states of O_2^+.

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[11] R.M. Badger, J. Chem. Phys. **3**, 710 (1935).