

ON THE BAND SYSTEMS AND STRUCTURE OF SiF.

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Introduction.

IN the course of an enquiry on the dissociation energies of certain molecules we came to deal with the SiF molecule whose spectrum has been investigated by Johnson and Jenkins.¹ Reference to this work showed that the nature of the electronic levels was left undecided and this is not surprising, since the work was done when the theory of band spectra was yet in the making. Johnson and Jenkins found a large number of bands, which on account of their appearance were divided into five groups, the so-called α , β , γ , δ and ϵ bands. They were further able to propose a vibrational analysis of the α - and β -bands, which showed, that these two systems involve a common final level, which being the lowest was regarded as the ground state of the molecule. This ground-level appears to have been regarded in literature as a $^2\Sigma$ level. Theoretical considerations which have been developed in recent years, we mean for instance the basic idea of the method of molecular orbitals of building up the configuration of the molecule by putting in electrons step by step in their energetical order, indicate, that the ground-level of the molecule SiF should rather be a $^2\Pi$ level. In view of this and the fact that the whole of the spectrum has not been systematised, we undertook a new vibrational analysis of these bands. It was not thought necessary to repeat the experiments, because of the accurate and careful data of Johnson and Jenkins. Further, the excellent reproductions of the bands, which they have published served us as well as original plates. We have been able to show that the analysis of the β -bands proposed by these authors happens to be numerically roughly correct, but the transition involved is $^2\Sigma \rightarrow ^2\Pi$. The analysis of the α -bands, however, needs considerable revision and shows that they should be regarded as a $^2\Pi \rightarrow ^2\Pi$ transition. The γ -bands which could not be analysed before

¹ R. C. Johnson and H. G. Jenkins, *P. R. S.*, 1927, 116(A), 327.

TABLE I.
Analysis of β -Bands.

v''	v'	0	1	2	3	4	5	6
0	P	34539.3 (10)	33693.7 (10)	32859.3 (4)	32030.7 (2)	31210.8 (0)		
	Q	555.7 (10)	708.4 (10)	870.1 (5)	043.1 (2)	..		
	P	701.8 (4)	856.1 (10)	33021.0 (3)	193.7 (0)	380.2 (0)		
	Q	716.6 (9)	869.3 (10)	031.9 (6)	(212.4) (2)	..		
1		35539.0 (8)	32212.4 (2)		
		557.5 (8)	33043.9 (6)	224.8 (2)	31411.1 (0)	
		703.8 (8)	c 34858.5 (2)	34019.8 (7)	193.0 (3)	376.2 (1)	..	
		719.1 (7)	c 871.9 (2)	032.3 (8)	204.1 (5)	391.9 (2)	578.5 (0)	
2	c	36532.2 (2)	35685.9 (4)	33217.4 (3)		31607.4 (0)
	c	548.3 (3)	34185.1 (3)	364.8 (2)	c 32405.5 (2)	764.1 (0)
		693.1 (3)	196.8 (4)	376.0 (4)	c 556.4 (1)	..
		711.3 (2)	863.9 (5)	c 569.2 (2)	..
3		36666.2 (2)	36666.2 (2)	35830.5 (1)
		685.2 (3)	685.2 (3)	848.5 (6)
		828.7 (3)	828.7 (3)	993.0 (2)	vd 35161.3 (1)	34348.3 (1)	33537.2 (0)	..
		846.4 (2)	846.4 (2)	36007.3 (2)	..	360.1 (1)	548.4 (1)	32745 (2)
4		36801.3 (2)	36801.3 (2)	36801.3 (2)	35976.2 (0)	..		
		820.7 (3)	820.7 (3)	820.7 (3)		
		964.1 (2)	964.1 (2)	964.1 (2)	36138.7 (0)	vd 35321.6 (2)		
		982.0 (1)	982.0 (1)	982.0 (1)	a 153.1 (0)	..		
5		36937.3 (1)	36937.3 (1)	36937.3 (1)	36937.3 (1)	
		955.9 (2)	955.9 (2)	955.9 (2)	d 37100.3 (2)	
		37100.3 (2)	37100.3 (2)	37100.3 (2)	116.8 (1)	..	vd 35480.8 (1)	
6		37074.1 (1)	37074.1 (1)	37074.1 (1)	..	37074.1 (1)		
		208.0 (0)	208.0 (0)	208.0 (0)	a	208.0 (0)		
		235.7 (0)	235.7 (0)	235.7 (0)	d	235.7 (0)		

are due to ${}^2\Sigma \rightarrow {}^2\Pi$. There is evidence to show, that the headless bands of the δ group also belong to this system. The final ${}^2\Pi$ level of all the three systems is the same, *i.e.*, the ground-level of the molecule. Only the bands in the ϵ system have not been classified but we have something to say about these later on. We now propose to give an account of the analysis, we have been able to make.

The β -Bands.

The analysis of this system is given in Table I. The bands form a well-defined system of close doublets in the region 3200 to 2680 A.U., and are degraded towards the shorter waves. In reality the close doublets are the P and Q heads associated with ${}^2\Pi_{1/2}$ and separated from a similar P and Q doublet of ${}^2\Pi_{3/2}$ by a frequency difference of about 161 cm.^{-1} . The analysis in the main yields similar constants to those given by Johnson and Jenkins because of the fact that the doublet separation is also roughly equal to the difference between the vibration frequencies of the initial and final states.²

The essential difference between the present analysis and the earlier one is, that whereas only two heads were ascribed to each band formerly, we now know that a ${}^2\Sigma \rightarrow {}^2\Pi$ transition should give rise to four heads, in this case two P and two Q heads, and these are shown in their proper places in the present analysis. This has necessitated a rearrangement of the vibrational quantum numbers used by Johnson and Jenkins and therefore a revision in the vibrational constants. Incidentally the present analysis does not indicate any pronounced perturbation, which according to the older one was present. The perturbations, if any, are only met with in the α -bands, where also it is difficult to decide this point because of the absence of Q heads, the data being obtained from R heads only. We believe that this rearrangement of the bands also removes the slight discrepancies in the isotopic observations, mentioned by Johnson and Jenkins.

The data for the mean vibrational differences of the ground state are given in Table VII later on together with those derived for the same level from other systems. The mean vibrational differences for the initial state are :—

² We cannot say anything definitely on the difficulty experienced by Johnson and Jenkins regarding the isotopic heads, because the data are not included in their paper. It is quite possible that the introduction of half quantum numbers will solve this difficulty especially if we remember that $(\rho-1)$ for Si^{28}F and Si^{30}F is fairly large (-0.0136) and ν_e will be shifted by about 80 cm.^{-1} .

TABLE II.
 $\Delta G'(v)$, β -Bands.

	0-1	1-2	2-3	3-4	4-5
P-P	999.5	990.8	980.2	973.2	961.4
Q-Q	1001.6	991.1	982.6	973.1	963.7

Using the values obtained from the Q heads the following equation is derived from the weighted means for the second differences:—

$$\nu_{\text{head}} = \left. \begin{matrix} 34555.7 \\ 716.6 \end{matrix} \right\} + (1006.4 v' - 4.8 v'^2) - (852.0 v'' - 4.7 v''^2).$$

The γ - and the δ -Bands.

The structure of the γ -bands is similar to that of the β -bands. Each band consists of two P and two Q heads and they appear as double-headed bands because of the overlap of successive sequences, the electronic separation, which is the same as in the β -bands, being greater than the difference between the two vibrational frequencies. Table III contains

TABLE III.
 Analysis of γ -Bands.

$v' \setminus v''$	0	1	2	3	4	5
0	P 39341.2 (3) Q 369.1 (5) P 503.2 (5) Q 531.5 (6)	38496.6 (2) 522.8 (5) 659.7 (3) 683.8 (5)	37664.4 (1) 685.3 (3) 827.3 (2) 847.2 (3)			
1		39370.3 (7) 401.7 (3) .. 562.3 (3)	38536.5 (3) 565.0 (2) 702.8 (2) 727.1 (2)	.. <i>vd</i> 37735.9 (1) 876.3 (2) 897.1 (2)		
2			.. 39430.0 (3) .. 591.4 (1)	38574.8 (2) 602.4 (2) 740.6 (2) 764.5 (2)	37760.7 (1) <i>d</i> 781.8 (1) 926.0 (1) 945.0 (1)	
3					38609.7 (2) <i>c</i> 638.8 (2) 775.9 (2) 800.7 (2)	37798.8 (1) .. 968.2 (1) ..
4						.. 38685.6 (2) 809.8 (2) <i>d</i> 834.5 (1)

an analysis of these bands. As will be seen from the data given in Table VII later, there is little doubt, that the final state of these bands is the same as that of the β -bands. The mean vibrational differences for the initial state are:—

TABLE IV.
 $\Delta G'(v)$, γ -Bands.

	0-1	1-2	2-3	3-4
P-P	873.8	864.3*	849.5	841.6*
Q-Q	879.3	865.8	855.9	

These data are not so numerous as in the β system and therefore the vibrational function derived is likely to be in error. For instance, the values marked with asterisks are each obtained by a single observation. Even in the Q heads already the 2-3 frequency is rather a mean of two values only, one of which is obtained from bands which are either confused or diffuse. Using the values weighted with due consideration to these facts, and taking for the final state the same function as for the β -bands, we obtain the following equation:—

$$v_{\text{head}} = \left. \begin{array}{l} 39369.1 \\ 531.5 \end{array} \right\} + (885.5 v' - 6.2 v'^2) - (852.0 v'' - 4.7 v''^2).$$

If, however, the data on the P heads are used, $\omega'x'$ comes out to be only 5.3 and this would make a big increase in the dissociation energy. We shall deal with this later. The electronic separation, obtained as a mean from the Q heads, comes out to be 161.8 cm^{-1} , as compared to 161.1 cm^{-1} the β -bands. This we take as evidence for the $^2\Sigma$ nature of the upper level though of course a $^2\Delta$ term with an insignificant electronic separation would just as well be valid.

We now come to the δ -bands which are described to be headless. The two vibrational functions of the γ -bands are close and the initial decreases more rapidly than the final so that already for the band (3, 0) and (3, 1) they will be practically identical and bands involving such transitions will be headless. The accuracy of measurement naturally cannot be very great and within such probable limits of inaccuracies it will be possible to include these headless bands in Table III. We have not included them, however, there, but the following Table V will show how the strongest of them could be classified on this basis.

TABLE V.
Classification of the Stronger δ -Bands.

ν	Intensity	Classification
39498	3	Q ₁ (4-4)
39674	2	Q ₂ (4-4)
40261	2	Q ₁ (2-1)
40337	1	Q ₁ (5-4)
40424	4	Q ₂ (2-1)
40510	4	Q ₂ (5-4)
41100	3	Q ₁ (3-1)
41276	5	Q ₂ (3-1)
41959	4	Q ₁ (3-0)
42121	1	Q ₂ (3-0)
39341.2	3	P ₁ (0-0)
39369.1	5	Q ₁ (0-0)

} Included in
Table III.

The α -Bands.

These bands are easily the most complicated. As shown in Table VI each band has again four heads. This apparently suggests a transition in which Λ changes by 1. This would mean the existence of Q heads which, however, are certainly not present as is clear from the partial rotational analysis given by Johnson and Jenkins. Further corroboration of this fact has been supplied recently by Badger and Blair³ who have reported a revision of the rotational analysis. This band, which is thus analysed, is that at 22886.2 cm.⁻¹. It consists of two strong branches, has an unmistakable null-point at a distance of about 18 cm.⁻¹ from the head and therefore cannot be the head of a strong Q branch which it would be if the transition involved a change of Λ . It is certainly therefore an R head and if any Q heads were present, they would have been near about the null-point. Such heads at an average distance of about 18 to 25 cm.⁻¹ are present for instance in the

³ R. M. Badger and C. M. Blair, *Phys. Rev.*, 1935, 47, 881.

TABLE VI.
Analysis of α -Bands.

ν'	0	1	2	3	4	5	6	7	8
0	<i>d</i> 23613.4 (6) 573.9 (10?) 448.4 (6) 411.6 (8)	22780.0 (4) 729.9 (9) 613.4 (6) 565.9 (10)							
1		23440.1 (5) 404.3 (8) 272.4 (5) 242.4 (7)	22608.1 (3) 568.1 (9) 442.9 (7) 405.4 (8)	<i>e</i> 21796.1 (2) 577.3 (3?) 20761.4 (4)				
2		23254.5 (3) 226.6 (7) 090.1 (7) 064.9 (8)	22434.3 (3) 399.2 (7) 267.5 (7) 236.8 (9)	22434.3 (3) 399.2 (7) 267.5 (7) 236.8 (9)	21620.3 (3) 577.3 (3?) <i>d</i> 455.5 (2) 413.3 (2)	.. 20773.4 (3) .. 610.7 (6)			
3			23066.4 (2) 041.8 (6) 22901.2 (5?) 886.2 (20)	23066.4 (2) 041.8 (6) 22901.2 (5?) 886.2 (20)	<i>c</i> 22252.8 (2) 222.9 (7) <i>d</i> 086.4 (7) <i>d</i> 061.0 (9) 21252.6 (1) 20448.4 (4)		
4					<i>c</i> .. <i>c</i> 22718.3 (10) ..	<i>d</i> 22061.0 (9) <i>c</i> 040.2 (7) <i>c</i> 21900.1 (6) <i>d</i> 878.1 (8) 21099.6 (2) <i>c</i> 20315.8 (1) <i>a</i> 284.1 (2)	
5					23485.1 (8) 451.5 (2)	<i>d</i> (21878.1) (8) 851.4 (6) 708.5 (3) 687.8 (5) 20910.7 (2) <i>a</i> 20111.9 (1)
6								21655.4 (4) 508.6 (2) <i>d</i> 497.1 (3)	

β - and γ -bands, but are completely absent here. According to our analysis this band is a (3, 3) band and the abnormal intensity is certainly due to the fact that it is not a single band but has superimposed upon it another band, probably a (4, 4) band with about the same wavelength.

The Q heads being ruled out, the transition must be one involving no change in Λ and since the final state of these bands is identical with that of the β - and γ -bands, the transition involved is ${}^2\Pi \rightarrow {}^2\Pi$. The existence of four heads in such a transition is unusual but is possible if the Ω selection rule no longer holds. This happens, when one of the terms approaches more to Hund's case *b*. We believe that such a condition obtains here and that the four observed heads are due to ${}^S R_{21}$, R_1 , R_2 , and ${}^Q R_{12}$ branches respectively. A similar case occurs in the ultra-violet bands of O_2^+ , where, however, the strong ${}^S R_{21}$ and ${}^Q R_{12}$ branches do not go to form heads. That they form heads in SiF is apparently due to the fact that the heads are formed at relatively high J values.

It is not obviously possible to deduce a strict value for the electronic separation of the R heads because this cannot be constant from band to band. If we take the mean separation between R_1 and R_2 heads, we obtain 132.2 cm.^{-1} which gives for the upper ${}^2\Pi$ state an electronic separation of $(161.1 - 132.2) = 28.9 \text{ cm.}^{-1}$. This incidentally shows, that the upper ${}^2\Pi$ state is also regular and not inverted. From the low magnitude of the electronic separations in both the upper state and particularly in the ground state, it appears as if the latter one, or, may be, both terms approach Hund's case *b*. The vibrational differences for the final state are included in the following Table VII along with those of the β - and γ -bands. From this comparison it can be concluded that the final levels of all the three systems are identical.

TABLE VII.
Comparison of $\Delta G''(v)$ values.

	0-1	1-2	2-3	3-4	4-5	5-6	6-7
β -Bands P-P	845.7	835.9	826.6	816.8	809.8	(792.3)	—
Q-Q	847.3	838.2	828.0	817.7	811.5	(800.8)	—
γ -Bands P-P	844.1	832.8	827.1	814.4			
Q-Q	847.0	836.5	828.7	820.1			
α -Bands R-R	839.5	833.7	823.1	817.8	808.4	(802.4)	(790.8)

The vibrational differences of the Q heads of the β - and γ -bands agree very well indeed and those of the α -bands generally as well as can be expected from the values which are obtained as means of all the four R heads. The value 839.5 for the first vibrational difference in these bands as compared with the same difference obtained in the other bands indicates, if real, a perturbation in the first two levels of the initial state of the system.

The mean vibrational differences for the initial state are given in the following table:—

TABLE VIII.
 $\Delta G'(v)$, α -Bands.

0—1	1—2	2—3	3—4	4—5	5—6
667.5	651.7	639.6	628.7*	601.8*	597.9*

On account of the absence of Q heads the mean differences thus obtained are not equally reliable and particularly those marked by asterisks are obtained from a few measurements only. It is quite likely therefore that the vibrational function derived from these values will be slightly in error. Due consideration to this fact will be given later when we come to discuss the dissociation products. Using for the final vibrational function that obtained from the more accurate data of the β -bands, we derive the following equation to represent the bands of the α system:—

$$\nu_{\text{head}} = \left. \begin{array}{l} 23613.4 \\ 573.9 \\ 448.4 \\ 411.6 \end{array} \right\} + (674.4v' - 6.9v'^2) - (852.0v'' - 4.7v''^2).$$

Unclassified Bands.

The analysis given includes all the bands in the β and γ systems of Johnson and Jenkins except one or two, which are very weak; most of the strong bands listed in the so-called δ system are shown also as part of the γ system and the weaker ones probably belong also to the same system. Among those listed in the α system all the strong ones are accounted for but there are a few with an intensity less than about 2 which cannot be fitted in the scheme. The bands thus unaccounted for are not only all weak but most of them are also diffuse or confused with other bands and some of them are measured approximately only. A more careful investigation would, we believe, be necessary to assign them properly either as main bands of the system or as isotopic heads.

The only system which we have not been able to analyse is the ϵ system. These bands are degraded towards the violet and very few of them are strong. We believe the data are not sufficient, but from the fact that they are degraded towards the violet, the vibrational frequency in the initial state will be bigger than that of the ground state, which, we believe, will be identical with that of the other systems. We offer further remarks about this system later.

Intensity Distribution.

The intensity distribution of all three systems is shown in Tables IX (*a* to *c*). In the β -bands the intensity distribution is roughly analogous to that shown in Fig. 16 (*a*) in Jevons' *Report*⁴ with a pronounced bias towards the initial level. This is in conformity with the greater energy of dissociation which the molecule has in the initial state. The α -bands, on the other hand, correspond to a distribution given in Fig. 16 (*c*) of Jevons' *Report* with a pronounced stability of the lower state. The γ -bands show an intensity distribution of the type given in Fig. 16 (*b*) of the above *Report*. On account of the near equality of the ω values, the bands are confined to a few long sequences, not involving big changes of v . This indicates that our interpretation of the headless bands is very probably correct. We believe also that the energy of dissociation of the upper state is more likely to be equal to or slightly bigger than that of the lower state, and not smaller than

TABLE IX.
Intensity Distribution.
(*a*) β -Bands.

$v' \backslash v''$	0	1	2	3	4	5	6
0	8	10	5	2	0		
1	8	2	8	5	2	0	
2	3	5		4	3	2	0
3		3	3	1vd	1	1	2vc
4			2	0	2vd		
5				2		1vd	
6					0		

⁴ W. Jevons, *Report on Band Spectra*, London, 1932, p. 69.

TABLE IX. (b) γ -Bands.

$v' \backslash v''$	0	1	2	3	4	5
0	5	4	2			
1		4	2	2		
2			2	2	1	
3					2	1
4						2

TABLE IX. (c) α -Bands.

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	8	8							
1		6	7	2	4				
2			6	7	3	5			
3				6	6	1	4		
4					8	8	2	2	
5					4		6	2	1
6								3	

it, as obtained from extrapolation of the above vibrational function. The correlation of the products of dissociation of the upper state to atomic terms also points in this direction, as will be seen later.

Dissociation Energy and Electronic Configuration.

The energies of excitation and dissociation of the observed terms of the molecule are given in volts together with the excitation energies of the dissociation products in the following Table X and in the diagram of Fig. 1.

TABLE X.
Dissociation and Excitation Energy.

Term	ν_0 (volts)	D (volts)	$\nu_0 + D' - D''$
X $^2\Pi$	0	4.77	0
A $^2\Pi$	2.91	2.04	0.18
B $^2\Sigma$	4.28	6.51	6.03
C $^2\Sigma$	4.88	3.90	4.01

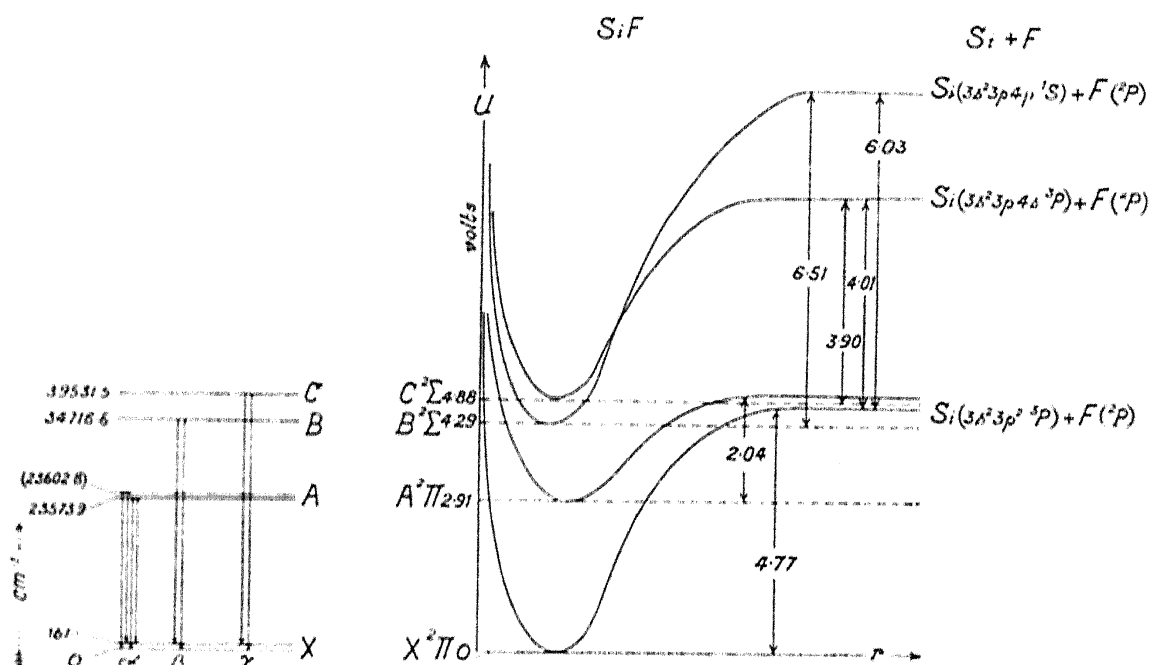


FIG. 1.

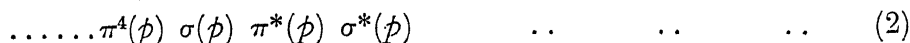
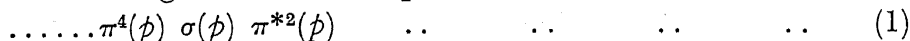
We now proceed to discuss the correlation of the molecular levels to those of the separated atoms and thus select the most probable electronic configurations of the molecule in its four states from the various possible ones. The ground state X $^2\Pi$ of the molecule arises from unexcited atoms Si ($3s^2 3p^2, ^3P$) + F ($2s^2 2p^5, ^2P$).

From these configurations we derive the following structure:

$$\dots \sigma^2(s) \sigma^{*2}(s) \pi^4(p) \sigma^2(p) \pi^*(p) \dots X^2\Pi.$$

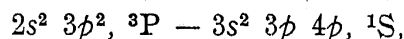
The level A $^2\Pi$ involves the same unexcited atoms; the difference of 0.18 volts between the dissociation products is well within the errors of extrapolation or, if real, might be attributed to the electronic separation

of one or both of the constituent atoms. It must, however, be remembered that the constants for this level are derived from the R heads and the vibrational frequency differences obtained are fewer as well as less satisfactory than those of the B $^2\Sigma$ and X $^2\Pi$ levels of the molecule. Still, there appears to be little doubt, that the curve runs to the same convergence limit as that of the ground-level. These considerations show that the electronic configuration of this state does not involve a change in the principal quantum number of the electrons. Furthermore, it cannot be the $\pi^*(p)$ electron, which without change in the principal quantum number can be transferred to the $\sigma^*(p)$ group only, because the resulting molecular term would then be $^2\Sigma$. Therefore we have only to consider the excitation of one of the inner p -electrons. The following are the three possibilities in this case:—

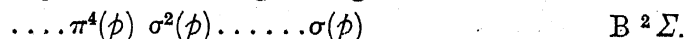


The first of these is to be ruled out because it does not give rise to a $^2\Pi$ level. It is difficult to choose between the possibilities (2) and (3) which are both probable. Since the energy of dissociation in this state is considerably less than in the ground state without an increase of the principal quantum number of the electrons, it is one of the bonding electrons, that is excited. From the point of view of the electron pair bond theory of linkage, the electron from one of the groups $\sigma^2(p)$ or $\pi^4(p)$ whichever contains a p -electron contributed by the Si atom, will be bonding, the second p -electron of Si being the odd electron in the group $\pi^*(p)$. From the other view-point both groups are non-promoted and therefore bonding.

The level B $^2\Sigma$ is interesting. The constants for this level are particularly more reliable than those for A $^2\Pi$ and C $^2\Sigma$. We expect therefore that the extrapolated energy of dissociation, which is derived from the constants deduced from the Q heads is accurate. It clearly indicates a strong increase in bond energy. From analogy with many other molecules, in which a similar situation obtains we ascribe this increase to the excitation of the odd $\pi^*(p)$ electron, which has been shown in numerous cases to have nothing to do with the linkage but to disturb it. Indeed the energy of 6.03 volts between the dissociation products of this and the normal state is in complete accord with 6.16 volts which is the difference

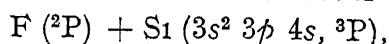


of Si. Accordingly the $\pi^*(p)$ odd electron is taken to one of the $\sigma(p)$ groups of the next principal quantum number, probably the non-promoted one. We therefore assign the following configuration to this level:—



This therefore furnishes another example in favour of the pair-bond view. Extending this view we should expect some other terms with increased energy of dissociation arising from configurations of the atom Si such as $3p\ 4s, {}^3P$ which also would give structures of the molecule in which the odd electron is excited. Such a molecular term originates at 4.9 volts (the energy of excitation of 3P) and if we assume a dissociation energy similar to that of $B\ {}^2\Sigma$, we obtain for the excitation of the molecule about 3 volts. It is not unlikely that the bands of the so-called ϵ system with 23898 cm^{-1} as one of its strongest bands belong to such a state. These bands are degraded towards the shorter waves, as we would expect them to be on account of increased energy of dissociation.

The $\Delta G'(v)$ values for the $C\ {}^2\Sigma$ level are not so numerous and therefore not so satisfactory as those of the β -bands. They should, however, be more reliable than those for the $A\ {}^2\Pi$ level because here we can deduce them from the Q heads. We remark here simply that the data on P heads yield for $\omega'x'$ 5.3 while those on Q heads give 6.2. The dissociation energy is extrapolated from the latter values and it appears as if it is slightly too low. As a matter of fact, there is no term in Si and of course none in F which can be correlated to 4.01 volts which is the excitation of the products of dissociation of this level. We therefore attribute this level to



which gives an excitation energy of 4.90 volts. Indeed, if we would use for $\omega'x'$ the value 5.3 obtained from data on P heads, we get a dissociation energy of 4.6 volts and an excitation energy of 4.7 volts for the products of dissociation. On this basis the electronic configuration would contain a $\sigma(s)$ electron of the next higher main quantum number which has been a p -electron in the $X\ {}^2\Pi$ level. It cannot be an electron from the $\sigma^2(p)$ group because the resulting configuration $\sigma\pi\sigma$ cannot give a ${}^2\Sigma$ level. Therefore it must be one of the promoted or non-promoted π -electrons. By assuming an excitation energy of 4.90 volts for the dissociation products the energy of dissociation of the $C\ {}^2\Sigma$ level becomes 4.81 volts. This value is almost identical if not higher than that for the ground-level. This is not improbable in view of the fact that the γ -bands are shaded towards the shorter wave side, which certainly means a decrease in the internuclear distance and probably, but not always, an increase of the bond energy. In view of this, we rather believe that it is the $\pi^*(p)$ electron, which is excited to the next higher $\sigma(s)$ group and the electronic configuration would then be the following:—



The theoretical implications will be discussed at greater length in a forthcoming paper.