

THE EMISSION SPECTRUM OF THE γ -SYSTEM OF SiF

by S. SANKARANARAYANAN and P. S. NARAYANAN, *Department of Physics, Indian Institute of Science, Bangalore*

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During the study of SiF₂ bands, it was found that under certain conditions the γ -system of SiF also could be obtained practically free from continuum and more bands than hitherto known were observed. A vibrational analysis of the observed bands of the γ -system of SiF yielded the following formula for the bands:

$$\begin{aligned} \nu_{cm-1} = & \frac{39351.7}{513.6} + 891.1(v' + \frac{1}{2}) - 6.06(v' + \frac{1}{2})^2 \\ & - 856.6(v'' + \frac{1}{2}) + 4.71(v'' + \frac{1}{2})^2 \end{aligned}$$

The upper state has been identified as a $^2\Sigma$ -state and the equilibrium internuclear distance in this state has been calculated to be 1.57 Å from the observed head-head separation data. The Franck-Condon factors for a few bands of this system as calculated by Bates's method are found to explain the observed features such as the termination of the v'' -progression ($v' = 0$) at (0, 2) band and the absence of the (2, 1) band. The most probable electron configuration for the upper state is also indicated.

1. INTRODUCTION

In the course of our investigation of the spectrum of SiF₂, the γ -system of SiF was observed free from continuum and in greater detail than studied by earlier workers. The references have been given in an earlier paper (Sankaranarayanan 1962). The γ -system of SiF has been analysed in the light of the additional data.

2. EXPERIMENTAL

The experimental arrangement used for recording the system of SiF was essentially the same as that described earlier, except for the fact that a cavity was blown just below the electrode to prevent the deposits produced during the discharge from obstructing the passage of light. The spectrum was recorded with a Hilger medium quartz spectrograph (dispersion of about 140 cm⁻¹ in the region of the spectrum) and also with a Hilger large quartz spectrograph E 185 having a dispersion of about 15 cm⁻¹ per mm at 2670 Å. The lower dispersion spectrogram was taken on Ilford Special Rapid plate while for the high dispersion instrument an exposure of 5 hours on Ilford Zenith Astronomical plate yielded a spectrogram in which the rotational structure

was clear but not of enough contrast for reproduction here. The wavenumbers of the sharp band heads of the medium spectrogram are accurate to $\pm 1 \text{ cm}^{-1}$ while the measurements of the diffuse heads are subject to an error of about $\pm 2 \text{ cm}^{-1}$.

3. RESULTS AND ANALYSIS

The γ -system recorded with the medium quartz spectrograph is reproduced in Fig. 1 (Plate I). Eleven new bands were obtained and Table I gives the band head data, the visual estimate of their intensities, the vibrational assignment and the classification of the various heads, the reason for this classification being given below. The data of Johnson and Jenkins (1927) are also included in Table I for comparison.

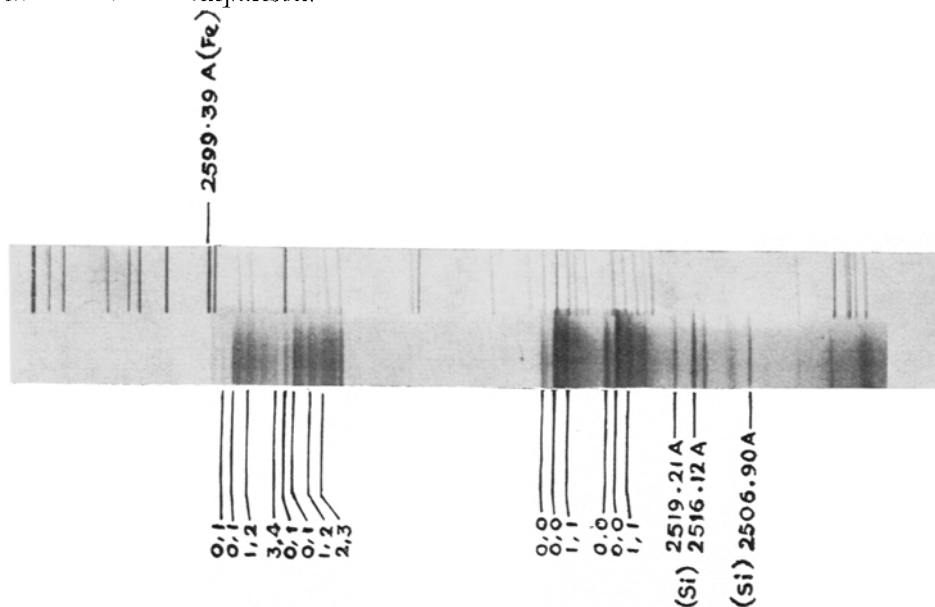


FIG. 1. The γ -system of SiF.
(Partial enlargement of medium quartz spectrogram)

Using the inner heads the following vibrational formula was derived :

$$\nu(\text{cm}^{-1}) = 39351.7 + 891.1(v' + \frac{1}{2}) - 6.06(v' + \frac{1}{2})^2 \\ 513.6(v'' + \frac{1}{2}) - 856.6(v'' + \frac{1}{2})^2 + 4.71(v'' + \frac{1}{2})^3$$

The band system origin ν_e and $w'_e x'_e$ differ from those given by Johns and Barrow (1958) probably because a few more Q heads were used in constructing the above relation. There is, however, close agreement between the other constants.

4. DISCUSSION

The separation of 161.9 cm^{-1} between the origins and of about the same magnitude between the inner heads agrees with the known spin-splitting of

TABLE I
The Bands of γ -System of SiF

ν Authors	Int.	ν Johnson & Jenkins (1927)	Vibra- tional assign- ment (ν' , ν'')	Classi- fication of head	ν Cal.	ν Obs. - ν Cal.
37662.1	2 <i>d</i>	37664.4	0, 2	P_{12}		
684.7	4	685.25	0, 2	P_2	37683.7	1
714.1	3 <i>d</i>	—	1, 3	P_{12}		
733.5	4	735.9	1, 3	P_2	733.3	-0.8
761.9	2 <i>d</i>	760.7	2, 4	P_{12}		
781.7	3	781.8	2, 4	P_2	782.2	-0.5
793.0	1 <i>d</i>	798.8	3, 5	P_{12}		
826.6	4	827.3	3, 5	P_2	827.5	-0.9
846.0	4	847.2	0, 2	Q_1	845.6	0.4
876.2	3	876.3	1, 3	P_1		
896.3	3	897.1	1, 3	Q_1	896.2	0.1
925.3	2	926.0	2, 4	P_1		
945.8	2	945.0	2, 4	Q_1		
968.0	2	968.2	3, 5	P_1		
989.0	1	—	3, 5	Q_1	989.4	-0.4
38496.8	2	38496.55	0, 1	P_{12}		
522.2	6	522.8	0, 1	P_2	38521.4	0.8
535.1	3 <i>d</i>	536.5	1, 2	P_{12}		
562.9	5	565.0	1, 2	P_2	562.6	0.3
573.8	3 <i>vd</i>	574.8	2, 3	I_{12}		
601.6	4	602.4	2, 3	J_2	601.2	0.4
609.5	3 <i>d</i>	609.7	3, 4	P_{12}		
636.4	4	638.8	3, 4	P_2	637.0	-0.6
646.0	2 <i>d</i>	—	4, 5	P_{12}		
659.5	5	659.7	0, 1	P_1		
38670.0	3 <i>d</i>	—	4, 5	P_2	38670.1	-0.1
683.4	8	38683.8	0, 1	Q_1	683.3	0.1
697.4	4 <i>d</i>	702.8	1, 2	P_1	—	—
726.1	6	727.1	1, 2	Q_1	724.6	1.5
742.9	3 <i>d</i>	740.6	2, 3	P_1		
763.2	5	764.5	2, 3	Q_1	763.1	0.1
773.0	3 <i>d</i>	775.9	3, 4	P_1		
797.4	4	800.7	3, 4	Q_1	798.9	-1.5
807.8	5	809.8	4, 5	P_1		
832.6	2	834.5	4, 5	Q_1	832.0	0.6
39335.2	4	39335.0	0, 0	P_{12}		
368.6	7	370.3	0, 0	P_2	39368.6	0
400.9	3	401.7	1, 1	P_2	400.4	0.5
430.0	2	403.0	2, 2	P_2	429.5	0.5
455.8	2	—	3, 3	P_2	455.9	-0.1
457.0	1	—	4, 4	P_{12}		
478.5	2	477.0	4, 4	P_2	479.6	-1.1
501.6	7	503.2	0, 0	P_1		
530.5	7	531.5	0, 0	Q_1	530.5	0
538.0	5	—	1, 1	P_1		
561.0	4	562.3	1, 1	Q_1	562.3	-1.3
590.9	2	591.4	2, 2	Q_1	591.4	-0.5
619.1	1 <i>d</i>	—	3, 3	Q_1	617.8	1.3
640.4	1 <i>vd</i>	—	4, 4	Q_1	641.5	-1.1
40247.8	1 <i>vd</i>	—	1, 0	P_2	40247.6	0.2
40407.2	1 <i>vd</i>	—	1, 0	Q_1	40409.5	-2.3

 d = diffuse vd = very diffuse

the ${}^2\pi$ state, which is the ground state of this molecule. Hence it is reasonable to suppose that this is the lower state of this system of bands. Also the present observations indicate that the spin-splitting of the upper state must be small. The upper state therefore is possibly a ${}^2\Delta$ or a ${}^2\Sigma$ state. Had it been a ${}^2\Delta$ state, the rotational structure should be more complicated than that indicated by the higher dispersion spectrogram.

There was no evidence for additional branches other than those expected for a ${}^2\Sigma-{}^2\pi$ transition indicated below and the rotational lines of even high rotational quantum numbers were found to be sharp. Since the w 's of the two states involved are nearly equal, the band heads are formed at a high rotational quantum number. It was therefore assumed that the upper level is a ${}^2\Sigma$ state and as it was found possible to explain nearly all the observed features of the spectrum, one is tempted to conclude that the identification is correct. The known relative abundance of the isotopes of Si precludes the possibility of isotope effect as a source of error in our analysis.

Since $A/B \simeq 279.6$ (A is the spin-coupling constant, B is the rotational constant), the ${}^2\pi$ state will be closer to Hund's case (*a*). In the case of violet degraded bands of a ${}^2\Sigma-{}^2\pi$ transition was shown by Gaydon (1944) that the head-forming branches are the P_{12} , P_2 , P_1 and Q_1 . Following his notation and neglecting Λ -type doubling, spin-splitting and the influence of the D -terms, the branches are given by

$$\nu(P_{12}) = \nu_0^{(1)} + \frac{3}{4}B' - (2B' + B_{eff}^{(2)'})J + (B' - B_{eff}^{(2)'})J^2$$

$$\nu(P_2) = \nu_0^{(1)} - \frac{1}{4}B' - B_{eff}^{(2)'}J + (B' - B_{eff}^{(2)'})J^2$$

$$\nu(P_1) = \nu_0^{(2)} + \frac{3}{4}B' - (2B' + B_{eff}^{(1)'})J + (B' - B_{eff}^{(1)'})J^2$$

$$\nu(Q_1) = \nu_0^{(2)} - \frac{1}{4}B' - B_{eff}^{(1)'}J + (B' - B_{eff}^{(1)'})J^2$$

It can be shown by simple differentiation that the heads are formed in the branches at the rotational quantum numbers

$$\frac{2B' + B_{eff}^{(2)'}}{2(B' - B_{eff}^{(2)'})}, \frac{B_{eff}^{(2)'}}{2(B' - B_{eff}^{(2)'})}, \frac{2B' + B_{eff}^{(1)'}}{2(B' - B_{eff}^{(1)'})}$$

and

$$\frac{B_{eff}^{(1)'}}{2(B' - B_{eff}^{(1)'})} \text{ respectively.}$$

Therefore the head-head separations P_2-P_{12} and Q_1-P_1 are given by

$$\frac{2B'B_{eff}^{(2)'}}{(B' - B_{eff}^{(2)'})} \text{ and } \frac{2B'B_{eff}^{(1)'}}{(B' - B_{eff}^{(1)'})} \text{ respectively.}$$

In the above expressions $B_{eff}^{(1)'} = B_v \left(1 - \frac{B_v}{A}\right)$ and $B_{eff}^{(2)'} = B_v \left(1 + \frac{B_v}{A}\right)$. B_{eff} 's were

calculated using the recent data of Verma (1962) for A and B and the value of α_e given by Johns and Barrow (1958). With the help of the values of B''_{eff} and the experimentally measured head-head separations, the B' values for the upper state were calculated. These results are given in Table II.

TABLE II

Band	$P_2 - P_{12}$	B'	$Q_1 - P_1$	B'	Mean B'
0, 0	33.4	0.60200	28.9	0.60093	0.6011
0, 1	25.4	0.60268	23.9	0.59998	
0, 2	22.6	0.59992	—	—	0.5952
1, 1	—	—	23.0	0.60116	
1, 2	27.8	0.59402	28.7	0.58889	
1, 3	19.4	0.59880	20.1	0.59312	
2, 3	27.8	0.58783	20.3	0.59278	
2, 4	19.8	0.59165	20.5	0.58615	0.5896
3, 4	26.9	0.58246	24.4	0.58085	0.5808
3, 5	—	—	21.0	0.57909	
4, 5	24	0.57925	24.8	0.57423	0.5767

A least square treatment of these data gave the values of B_e and α_e for the upper state as 0.6045 and 0.0062 respectively. The internuclear distance r_e for the upper state was calculated using the relation

$$B_e = \frac{27.983 \times 10^{-40}}{\mu r_e^2}$$

and the r_e -value comes out to be 1.57 Å in good agreement with the value of Johns and Barrow (1958). With these data the Franck-Condon factors $q_{v'v''}$ for a few bands were calculated by Bates's method (Bates 1952) and the values are given in Table III.

TABLE III
Franck-Condon Factors

$v'' \backslash v'$	0	1	2	3	4
0	0.876	0.109	0.019	0.000	
1	0.117	0.663	0.183	(0.017)	
2	0.004	0.007	(0.476)		
3	0.000	(0.027)			

Values in parenthesis are on the basis of harmonic oscillator approximation. Probable error on account of this approximation is negligible for the (2, 2) band and is about 2% for the other two bands.

It is evident from the tabulated values of the F.C. factors that the observed features of the γ -system of SiF such as the termination of the v'' -progression ($v' = 0$) at (0, 2) band and the absence of the (2, 1) band are in satisfactory agreement with what one would theoretically expect.

5. ELECTRONIC CONFIGURATION

The possible low-lying electron configuration of SiF and the states they can yield have been considered by Asundi and Samuel (1936), Johns and Barrow (1958) and Verma (1962). While the configurations of the $A(^2\Sigma^+)$ and $B(^2\Sigma^+)$ states have been identified, the evidence for the C state has so far been inconclusive. The present observation indicates that it is in all probability a $^2\Sigma^-$ state arising from the electron configuration $(w\pi)^4(x\sigma)(v\pi)^2$. The above configuration can yield a $^4\Sigma^-$ state also and Verma (1962) has shown that the η -bands of SiF arise from a $^4\Sigma^- \rightarrow \chi^2\pi$ transition. Therefore the higher value of ν_e of the γ -system and the non-observation of $C-A$ ($^2\Sigma^+$) transition by Johns and Barrow support the present identification of the upper state of the γ -system.

The spin-orbit coupling in the ground state of the silicon halides may be used to get an estimate of the localization of the $(v\pi)$ orbital. The spin-orbit coupling constant A_{SiX} of the ground state can be approximately taken to be

$$A_{SiX} = C_1^2 |A_{Si}| + C_2^2 |A_X|; C_1^2 + C_2^2 = 1$$

where the A_{Si} and A_X are the spin-orbit coupling constants of the Si and halogen atoms. Since $|A_X|$ is much larger than $|A_{Si}|$ though not to the same extent as in carbon halides (Dixon and Kroto 1963) A_{SiX} can be employed to give the values of C_1^2 and C_2^2 . Using the available data for SiF, SiCl and SiBr (Herzberg 1950; Verma 1962; Bacher and Goudsmit 1932), one finds the C_2^2 values to be 0.445, 0.260 and 0.144 respectively. If we neglect the overlap between the silicon and halogen p orbitals, the above values show that the $v\pi$ orbital is not completely localized either on Si or on the halogen. It must be considerably anti-bonding in character. By the same line of argument $(w\pi)$ also will be only considerably but not completely bonding. This in a way justifies the assignment by Johns and Barrow of the electronic states $C'^2\pi$ and $D^2\pi$ to the electronic configuration $(w\pi)^3(x\sigma)^2(v\pi)^2$. Since there is a shortening of the bond in the upper state C arising from an excitation of the $(x\sigma)$ electron to the $(v\pi)$ orbital, it is to be concluded that the $(x\sigma)$ orbital is more anti-bonding in nature than the $(v\pi)$ orbital in this case. Recently, investigating the spectrum of SiCl in the region 2830–2760 \AA , Verma (1964) has shown that it arises from a $B'^2\Delta - \times^2\pi$ transition. By a comparison of the energies of the different states of SiCl and SiF he concluded that the $B'^2\Delta$ state of SiCl must have the same electron configuration as that suggested here for the $C(^2\Sigma^-)$ state of SiF. To be sure, in SiCl

also one finds that there is a shortening of the bond in the upper state (Verma 1964). The magnitudes of T_e value of the two analogous states is also in support of the above conclusion.

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