

The $C^2\Pi-X^2\Sigma$ system of SrF molecule

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Abstract. The spectrum of the $C^2\Pi-X^2\Sigma$ system of SrF molecule has been investigated under high resolution. The rotational structure in the (0, 0) band has been analysed and the rotational constants for the $C^2\Pi$ state have been obtained. The vibrational analysis of this system has been carried out using the band heads from the high resolution spectrogram and also the band origins and the precise vibrational constants have been reported for both the participating states.

Keywords. Concave grating spectrograph; vibrational constants; rotational constants; spin splitting; microwave optical double resonance (MODR); laser fluorescence; head-head separation.

1. Introduction

The spectrum of the $C^2\Pi-X^2\Sigma$ system of SrF molecule extending from 3600 to 3795 Å was first observed by Johnson (1929) and subsequently by Fowler (1941) in absorption. These authors performed the vibrational analysis of these bands and surmised that they are due to the transition $^2\Pi-^2\Sigma$, where $^2\Sigma$ is the ground state of this molecule. Novikov and Gurvich (1967), later on recorded these bands in emission and modified the previous vibrational numbering reported by Fowler (1941). The spin orbit coupling constant in the $C^2\Pi$ state was found to be $\sim 60 \text{ cm}^{-1}$ and on this basis they surmised it to belong to the intermediate coupling between Hund's case (a) and case (b).

The $B^2\Sigma-X^2\Sigma$ and $A^2\Pi-X^2\Sigma$ systems of this molecule has recently been studied extensively using the laser fluorescence and microwave optical double resonance (MODR) techniques by Steimle *et al* (1977, 1978). A comparison of the vibrational constants for the ground state reported by these workers are found to be much different from the constants given by Novikov and Gurvich (1967). It was therefore considered worthwhile to record the spectrum of the C-X system of this molecule under high resolution and determine the accurate vibrational and rotational constants.

In the present analysis the vibrational assignments of Novikov and Gurvich (1967) has been confirmed and a large number of vibrational heads have been attributed to the same system for the first time. A precise set of molecular constants for the $C^2\Pi$ state has been obtained.

2. Experimental

The spectrum of the C-X system of SrF molecule was excited in a copper arc running at 220 V dc and 2.5 to 5.0 amp current. The spec-pure sample of SrF₂ (BDH 99.9%) was used in excitation. The spectrum was photographed in the second order of a 10.6 meter concave grating spectrograph with 0.33 Å/mm dispersion for a period of 3 hr. Iron arc lines were used as the standard for measurement. The spectrum was measured on a comparator with 10⁻⁴ mm least count.

Bands belonging to only two sequences *viz* (0, 0) and (0, 1) could be recorded under high resolution. Though the third sequence (1, 0) also appears under low resolution, its intensity is very poor and could not be recorded on the high resolution instrument.

3. Results and discussion

3.1 Description of the spectra

Since the transition of this system is well known ²Π-²Σ with the spin orbit coupling constant in the ²Π state equal to ~60 cm⁻¹, each band will split into two sub-bands separated by 60 cm⁻¹. In the presence of appreciable spin splitting in the ²Σ state six branches are expected to be present in each sub-band. Out of these the two branches namely ^SR₂₁ and R₂ in the ²Π_{3/2}-²Σ sub-band and R₁ and Q₁ in the ²Π_{1/2}-²Σ sub-band would form the heads, if the bands are red-degraded. A close inspection of the structure shows that all the four heads are present in each intense band in our spectrogram, whereas only a few heads could be marked in weak bands. The vibrational structure of 0-0 sequence is shown in figure 1.

There are only two series of rotational lines present in each sub-band of the (0, 0) band; however the intensity of (0, 1) band is very weak and the rotational structure in this band is not clear for measurements. The structure of only (0, 0) band could therefore be analysed.

3.2 Rotational analysis

Only two branches could be observed in the ²Π_{3/2}-²Σ sub-band as well as in the ²Π_{1/2}-²Σ sub-band. In the ²Π_{3/2}-²Σ sub-band the intensity of the ^SR₂₁ lines is too weak to be measured and the R₂ branch lines appear to die out after head formation; therefore there should be four branches Q₂, ^QR₁₂, P₂ and ^PQ₁₂ in the structure. However, the spin splitting in the ground state is very small (0.00245 cm⁻¹) and the spin components are expected to be resolved at very high *J* values. The branches in the structure are therefore expected to be Q₂ and P₂. Similarly in the ²Π_{1/2}-²Σ sub-band only ⁰P₁₂ and P₁ branches are observed. The R₁ branch lines are heavily overlapped by the atomic lines of strontium and the Q₁ branch dies out after the head formation.

Since the rotational constants for the ground state are known accurately, *J* assignments of the rotational lines could be made easily. The rotational constants in the ²Π_{3/2}-²Σ sub-band were estimated by graphical method and finally refined by the least square method. However in the ²Π_{1/2}-²Σ component the branches known are

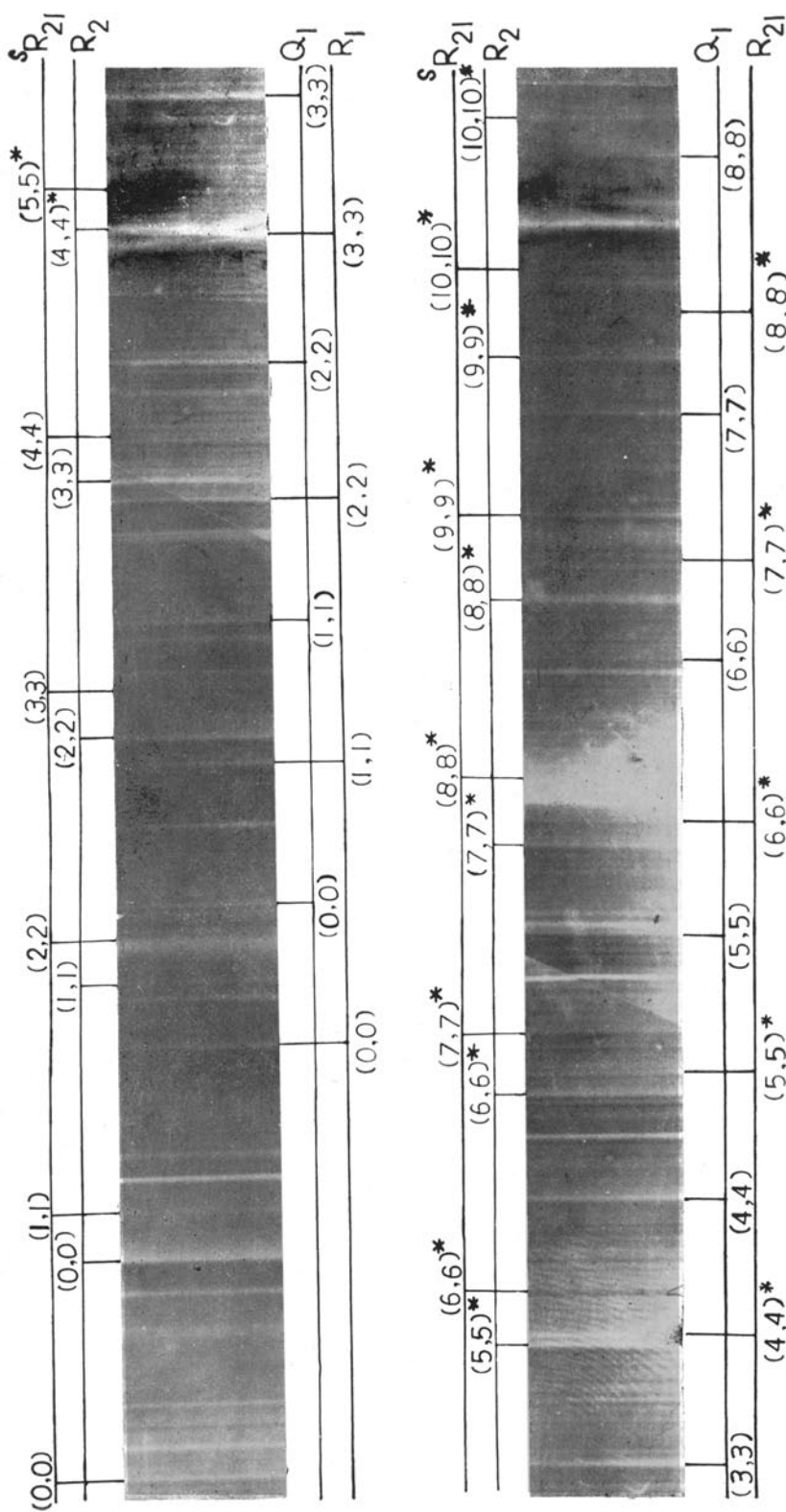


Figure 1. Vibrational structure in the 0-0 sequence of the $C^2\Pi-X^2\Sigma$ system of SrF molecule. Asterisk indicates newly observed heads.

${}^0P_{12}$ and P_1 ; therefore no combination difference of these lines could be made. At the same time in this component another constant called Λ -doubling is expected to be effective. Hence, for the determination of molecular constants for ${}^2\Pi_{1/2}$ component the usual method (Herzberg 1950) could not be used and we proceeded as follows:

The rotational constants for ${}^2\Pi_{1/2}$ component were estimated using the relation

$$B_{\text{eff}} = B_v \left(1 \pm \frac{B_v}{A\Lambda} \right), \quad (1)$$

and the head-head separations,

$$R_1(H) - Q_1(H) = 2B'_v{}^{(1)} - q - \frac{[(4B'_v{}^{(1)} - \gamma'')(2B'_v{}^{(1)} - q)]}{(4B'_v{}^{(1)} - B''_v)}. \quad (2)$$

The constants thus obtained for the excited state were minutely adjusted such that they fairly reproduce the branch lines P_1 and ${}^0P_{12}$. Final constants obtained in both the components reproduce the branch lines within our experimental error. The head-head separation calculated using the present constants in the two components is 24.33 cm^{-1} and 37.73 cm^{-1} which agree with the experimental values of 24.35 cm^{-1} and 37.73 cm^{-1} respectively. The rotational structure is resolved in only one band (0, 0), and therefore, we used the head-head separation data again to estimate α_e value in the excited state. Taking the head-head separation, the values of B''_v , γ and q were determined by estimating $B'_v{}^{(1)}$ (for $v = 1, 2, 3, 4 \dots 10$) and it was found that their successive differences (*i.e.* $B_0 - B_1, B_1 - B_2, B_2 - B_3 \dots$) are approximately of the order of 0.0014 cm^{-1} which is the α_e value for the ${}^2\Pi$ state. The equality of these differences supports the correctness of our calculation. We have also estimated the α'_e value using the Pekeris relation

$$\alpha_e = \frac{6(\omega_e x_e B_e^3)^{1/2} - 6B_e^2}{\omega_e}, \quad (3)$$

and obtained a value of 0.0012 cm^{-1} which agrees with the value of $\alpha_e = 0.0014 \text{ cm}^{-1}$. The B_e value for $C^2\Pi$ state now comes out to be 0.24636 cm^{-1} .

3.3 Vibrational analysis

Novikov and Gurvich (1967) performed the vibrational analysis of this system using their low resolution band head data. Although they used the Q_1 head data, their constants for the ground state are very much different from the constants reported by Steimle *et al* (1977), which are believed to be more accurate.

In the present work we used the high resolution band head data and fitted the values of $\Delta G'(v'+\frac{1}{2})$ and $\Delta G''(v''+\frac{1}{2})$ by least square to obtain precise vibrational constants. We also included the higher order anharmonicity constants $\omega_e y_e$ and $\omega_e z_e$ in the $\Delta G(v+\frac{1}{2})$ equations. The vibrational constants thus obtained can be well represented by the expression

$$\begin{aligned} \nu_Q(v', v'') &= 27382.9296 + 452.4285(v' + \frac{1}{2}) - 1.51049(v' + \frac{1}{2})^2 \\ &\quad - 0.037791(v' + \frac{1}{2})^3 + 0.001061(v' + \frac{1}{2})^4 - 500.55(v'' + \frac{1}{2}) \\ &\quad + 2.175(v'' + \frac{1}{2})^2 - 0.0005(v'' + \frac{1}{2})^3. \end{aligned}$$

This equation is found to reproduce the Q_1 head data within the error $\pm 0.1 \text{ cm}^{-1}$. However the constants for the $X^2\Sigma$ state thus obtained differ from the constants reported by Steimle *et al* (1977). The reason for this discrepancy is that the Q heads in different bands are formed at different J values; therefore, even if one uses the most accurate band head data, the vibrational constants thus determined will differ from the true equilibrium constants. Therefore no great weight can be attached to the constants determined by fitting the band head data. The band origins are therefore essential to obtain reliable values of the vibrational constants. We have therefore calculated the band origins of a large number of bands using the head origin separation formula for Q_1 heads,

$$\nu_{Q_1}(H) - \nu_0 = \frac{q}{4} + \frac{\gamma''}{4} + \frac{B_v''}{4} - \frac{\left(B_v^{(1)} + \frac{q}{2} - \frac{\gamma''}{2}\right)^2}{4(B_v^{(1)} - B_v'')} \quad (4)$$

$B_v^{(1)}$ and B_v'' are the rotational constants for different levels.

The origin of different bands, thus calculated were used to determine $\Delta G'(v'+\frac{1}{2})$ and $\Delta G''(v''+\frac{1}{2})$ values. These values were finally fitted by the least squares procedure again. The expression thus obtained is,

$$\begin{aligned} \nu_0(v', v'') = & 27379.4173 + 454.2245 (v'+1/2) - 1.6532 (v'+1/2)^2 \\ & - 0.01516 (v'+1/2)^3 + 0.000256 (v'+1/2)^4 - 501.92 (v''+1/2) \\ & + 2.1651 (v''+1/2)^2 - 0.00473 (v''+1/2)^3 + 0.00003 (v''+1/2)^4. \end{aligned} \quad (5)$$

The ground state vibrational constants thus obtained are $\omega_e'' = 501.92 \text{ cm}^{-1}$ and $\omega_e'' x_e'' = 2.1651 \text{ cm}^{-1}$, which are within the experimental error limit of the earlier values $\omega_e'' = 502.4(7) \text{ cm}^{-1}$ and $\omega_e'' x_e'' = 2.27(13) \text{ cm}^{-1}$, obtained by Steimle *et al* (1977) using laser fluorescence excitation technique. This supports the correctness of our analysis and the values of vibrational and rotational constants.

3.4 Electron configuration

The ground state of SrF molecule according to molecular orbital theory can be given as,

$$(z\sigma)^2 (\omega\pi)^4 (y\sigma) \dots {}^2\Sigma^+ \quad (6)$$

few low lying excited states of this molecule are,

$$(z\sigma)^2 (\omega\pi)^4 (np\pi) \dots {}^2\Pi \quad (7)$$

$$(z\sigma)^2 (\omega\pi)^4 (np\sigma) \dots {}^2\Sigma \quad (8)$$

$$(z\sigma)^2 (\omega\pi)^3 (y\sigma) (np\sigma) \dots {}^2\Pi, {}^2\Pi, {}^4\Pi \quad (9)$$

Here $(y\sigma)$ orbital is of nonbinding nature and is localised on the $5s$ orbital of Sr. Excitation of an electron from $(y\sigma)$ to $np\pi$ which in the present case is also a nonbonding type and mainly localised on $5p$ orbital of Sr gives a ${}^2\Pi$ state of nearly same frequency. A similar case is with $(np\sigma)$ configuration which gives a ${}^2\Sigma$ state. These

states are represented by A and B states of this molecule. The excitation of an electron from bonding orbital ($\omega\pi$)⁴ to nonbonding orbital ($np\sigma$) should give a decrease in the frequency. The $C^2\Pi$ state of this molecule perhaps arises from this configuration.

4. Conclusion

The high resolution spectrogram enabled us to mark many new heads in known bands which could not be marked by Novikov and Gurvich (1967). The measurements of many bands given by Fowler (1941) and Novikov and Gurvich (1967) were improved even upto few wavenumbers. The vibrational assignments of R_1 head in (4, 4), (5, 5) and (6, 6) bands made by Novikov and Gurvich (1967) were found incorrect. Actually they are R_2 heads of (5, 5), (6, 6) and (7, 7) bands. The wavenumbers of different heads alongwith their band origins ($\nu_0^{(1)}$) are given in table 1. The regularity in ΔG values supports our analysis. The wavenumber of rotational lines alongwith their J assignments are given in table 2 and the molecular constants for the two states are given in table 3. The rotational and vibrational constants reported by different workers are also compared in the same table. One can see that the present molecular constants are in good agreement with the constants reported by the laser fluorescence technique (Steimle *et al* (1977)), whereas they are much different from the values reported by Novikov and Gurvich (1967). For the first time we could report the B_e , a_e and Λ -doubling in the $C^2\Pi$ state of this molecule. These constants are found to reproduce the branch lines, band heads as well as the head-head separation to within $\pm 0.1 \text{ cm}^{-1}$.

Table 1. Vibrational assignment of the band heads in the $C^2\Pi-X^2\Sigma$ system of SrF molecule (cm^{-1}).

Band	Head	Frequency	Origin	Band	Head	Frequency	Origin
(0, 0)	$^S R_{21}$ R_2 R_1 Q_1	27457.46 27419.73 27383.38 27359.03	27355.69	(6, 6)	$^* S R_{21}$ $^* R_2$ $^* R_1$ Q_1	27192.48 27159.98 27114.23 27089.59	27086.05
(1, 1)	$^S R_{21}$ R_2 R_1 Q_1	27411.50 27372.28 27335.07 27312.12	27312.12	(7, 7)	$^* S R_{21}$ $^* R_2$ $^* R_1$ Q_1	27149.58 27118.87 27071.73 27046.60	27043.00
(2, 2)	$^S R_{21}$ R_2 R_1 Q_1	27365.94 27330.35 27290.32 27266.32	27263.10	(8, 8)	$^* S R_{21}$ $^* R_2$ $^* R_1$ Q_1	27106.65 27077.60 27029.00 27003.98	27000.29
(3, 3)	$^S R_{21}$ R_2 R_1 Q_1	27322.69 27287.18 27244.95 27221.32	27218.03	(9, 9)	$^* S R_{21}$ $^* R_2$ $^* R_1$ Q_1	27063.40 27037.46 26986.30 27961.52	26957.73
(4, 4)	$^* S R_{21}$ $^* R_2$ $^* R_1$ Q_1	27280.04 27244.00 27199.96 27176.76	27173.40	(10, 10)	$^* S R_{21}$ $^* R_2$ R_1 Q_1	27020.35 26997.60 26919.50	

Table 1. (Contd.)

Band	Head	Frequency	Origin	Band	Head	Frequency	Origin
(5, 5)	*S _{R₂₁} *R ₂ *R ₁ Q ₁	27237·00 27201·58 27156·29 27133·01	27129·58	(11, 11)	S _{R₂₁} R ₂ R ₁ Q ₁	— — — 26878·05	
(0, 1)	S _{R₂₁} R ₂ R ₁ Q ₁	— — 26886·65 26862·58	26858·09	(6, 7)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26687·77 26654·19 26619·42	26613·80
(1, 2)	S _{R₂₁} R ₂ R ₁ Q ₁	— — 26846·65 26820·31	26815·68	(7, 8)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26649·28 26617·21 26580·79	26574·90
(2, 3)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26852·78 26807·13 26778·71	26773·92	(8, 9)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26609·47 26580·06 26542·40	26526·20
(3, 4)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26811·45 26768·73 26738·02	26733·05	(9, 10)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26570·04 26544·77 26504·41	26497·86
(4, 5)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26770·00 26730·00 26698·35		(10, 11)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26531·53 26509·30 26466·00	
(5, 6)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26728·30 26692·12 26658·43	26653·05	(11, 12)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26493·52 26474·60 26428·10	
(12, 13)	S _{R₂₁} *R ₂ R ₁ Q ₁	— 26456·05 26439·60 26391·73		(14, 15)	S _{R₂₁} R ₂ R ₁ Q ₁	— — 26371·96 26319·35	
(13, 14)	S _{R₂₁} R ₂ R ₁ Q ₁	— — 26405·40 26355·48		(15, 16)	S _{R₂₁} R ₂ R ₁ Q ₁	— — 26338·26 26283·85	

*Newly observed heads.

Table 2. Vacuum wavenumbers and J assignments of the rotational lines in the (0, 0) band ($\nu_{00}^{(1)}=27359.69\text{ cm}^{-1}$ and $\nu_{00}^{(2)}=27414.88\text{ cm}^{-1}$).

J	$P_1(J)$	${}^oP_{12}(J)$	$P_2(J)$	$Q_2(J)$
6.5		27350.38		
7.5		49.54		
8.5		48.75		
9.5		47.98		
10.5		47.38		
11.5		46.28		
12.5		45.39		
13.5		44.52		
14.5		43.65		
15.5		42.76		
16.5		41.79		
17.5		41.17		
18.5		40.06		
19.5		38.96		
20.5		38.11		
21.5		37.05	27397.25	
22.5		36.11	96.40	
23.5		35.18	95.53	
24.5		34.15	94.65	
25.5		33.26	93.70	
26.5		32.26	92.85	
27.5		31.23	91.82	
28.5		—	90.94	
29.5		—	90.01	
30.5		28.10	89.00	
31.5	27342.92	27.06	88.05	
32.5	42.35	26.86	87.22	
33.5	41.81		86.10	
34.5	41.25		85.25	
35.5	40.70		84.15	
36.5	27340.06			
37.5	39.38			
38.5	38.86			
39.5	38.22			
40.5	37.55			
41.5	36.82			
42.5	36.12			
43.5	35.43			
44.5	34.89			
45.5	34.05			27396.60
46.5	33.41			96.05
47.5	32.65			95.44
48.5	31.93			94.80
49.5	31.26			94.28
50.5	30.52			93.75
51.5	29.79			93.18
52.5	28.95			92.48
53.5	28.10			91.85
54.5	27.43			91.23
55.5	25.86			—
56.5	26.76			90.05
57.5	25.00			89.44
58.5	24.27			88.92
59.5	23.32			88.20
60.5	22.48			87.60
61.5				86.98
62.5				86.30
63.5				85.52

Table 3a. Rotational constants for the $C^2\Pi-X^2\Sigma$ system of SrF molecule.

State	B_e	a_e	$D_e \times 10^7$	γ	a
$C^2\Pi_{1/2}$	0.24481 ^a	0.0014 ^b	2.51	—	0.005474
$C^2\Pi_{3/2}$	0.24651 ^a	0.0014 ^b	2.51	—	—
$X^2\Sigma^c$	0.250533	0.001546	2.49	0.0025	—

^aValue of B_0 .^bEstimated value using head-head separation.^cThe rotational constants for this state have been fixed the same as obtained by Steimle *et al* (1977) by the MODR analysis of the $B^2\Sigma-X^2\Sigma$ system of this molecule.Table 3b. Vibrational constants for the $C^2\Pi-X^2\Sigma$ system of SrF molecule.

Constants	Present	Steimle <i>et al</i> (1977)	Novikov and Gurvich (1967)
ν_e	27379.4173	—	27358.80
ω'_e	454.2245	—	448.0
$\omega'_e x'_e$	1.6532	—	1.72
$\omega'_e y'_e$	-0.01516	—	—
$\omega'_e z'_e$	0.000256	—	—
ω''_e	501.92	502.4(7)	498.0
$\omega''_e x''_e$	2.1651	2.27(21)	2.15
$\omega''_e y''_e$	0.00473	—	—
$\omega''_e z''_e$	-0.00003	—	—

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