

# Diatomic Molecule 'S<sub>2</sub>' of Astrophysical Interest: Potential Energy Curves, Franck Condon Factor and Dissociation Energies

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**Abstract-** Franck Condon factors for transitions connecting  $v' = 3$  and  $v' = 4$  vibrational levels of the  $B^3\Sigma_u^-$  state of  $S_2$  to the ground state  $X^3\Sigma_g^-$  state, have been calculated by, first calculating the Morse wave function which in turn, are, used to evaluate the overlap integral employing Numerov method of numerical integration. The results are very close to the experimental values. This fact prompted us to undertake, for the first time, the calculation of Franck Condon factors, for the Rydberg transitions of C-X, E-X, H-X and I-X band systems of  $S_2$  molecule in the VUV region. Using Morse Potential, numerical integration procedure is followed to evaluate these transition probability parameters. The derived absolute transition probabilities are compared with literature values.

Using Universal relation, dissociation energy of E, H and I electronic states are calculated as 14873, 2795 and  $8418\text{ cm}^{-1}$  respectively. These values, in turn, are used to draw RKR curves for the first time. Dissociation of electronic states E and H into  $^1S + ^1D$  and I into  $^1S + ^1S$  atomic states, have been observed.

**Keywords-** Diatomic Molecules, Franck Condon Factor, Intensity, Inter-nuclear Distance, RKR curve.

## I. INTRODUCTION

A precise knowledge of Franck Condon (FC) factors and related quantities are essential for an understanding of physico-chemical conditions of the emitting sources and for the calculation of many important data for the molecules e.g., radiative life times, vibrational temperatures and kinetics of energy transfer. Also, the transition probability parameters such as FC factors are required for diagnostic applications in astro-physics, astrochemistry and allied subjects. Furthermore, in order to interpret stellar spectra with laboratory studies, such theoretical calculations are equally important. The intensity measurements of various bands appearing in different electronic transitions along with the calculations of FC factors

help us also to understand the variation of electronic transition moment  $R_e$ .

On the other hand, the dissociation is prime factor in the various phenomena in diatomic molecules. Therefore, astrophysicists, chemists and spectroscopists are concerned with the determination of reliable values of dissociation energies of diatomic molecules. However, spectroscopic data for most of the diatomic molecules is available for the vibrational levels which are considerably below the dissociation limit. So different extrapolation methods [1-4] and fitting of empirical potential functions to RKR curves [5-8], have been employed to find the dissociation energy of diatomic molecules. In view of its importance, dissociation energy of various electronic states of  $S_2$  molecules are determined by universal relation given in reference [9]

The experimental diatomic molecular studies of sulphur- which has assumed great importance because of its occurrence in the interstellar medium, have been taken up intensively in our laboratory, particularly in the vacuum ultraviolet (VUV) region; therefore,  $S_2$  spectra is the subject matter of this communication.

Earlier work by Meyer and Crosley[10], utilized atomic line excitation of individual  $v'$  J' levels of the  $B^3\Sigma_u^-$  state of  $S_2$ , to obtain the FC factors  $q_{3,v'}$  and  $q_{4,v'}$  for  $v'=3, 4$ . Their values for  $v''=0$  through 10 that were based on experimental studies did not support the earlier analytical results calculated using the Morse potential [11] and RKR curve[12]. We have calculated the same FC factors using Leroy's program [13]. A close agreement of our results with the experimental values of Meyer and Crosley, prompted us to undertake such studies for the transitions E, H, I -X of  $S_2$ , for the first time, despite these transitions result in small progressions consisting of two or three bands.

Furthermore, the dissociation energy of the state E, H and I have been calculated using the Universal relation [9]. These values together with the dissociation of  $X^3\Sigma_g^-$  to

$S(^3P_2)+S(^3P_1)$ [9] and the atomic states of Sulphur have led us to show that E and H states dissociate into  $^1S + ^1D$  and I into  $^1S + ^1S$ .

## II. FRANCK CONDON FACTORS

The intensity of each individual transition between vibrational levels of an allowed electronic transition is governed by the overlap of vibrational probability factors in the upper and lower states, termed FC factors, which depend upon the geometry changes in the upper and lower electronic states and can be given as the square of the overlap integral,

$$q_{v',v''} = 1 \int \psi_{v'} R \psi_{v''} dr \quad I^2 \dots \dots \dots (1)$$

where  $\psi_{v'}$  and  $\psi_{v''}$  are the vibrational wave functions for the upper and lower electronic states respectively.

For a proper understanding of the intensity distribution in a band system of the molecules, it is necessary to choose a suitable potential. The Morse potential [14], which yields accurate FC factors for a vibrational transition involving low quantum numbers, is used in the present work.

Morse Wave functions are calculated for every observed level of each state of E-X, H-X and I-X band systems of  $S_2$  molecule at intervals of  $0.0002 \text{ \AA}^\circ$ . The necessary molecular constants are taken from literature [9,15-17,18] and are given in Table 1. Once the appropriate wavefunctions are obtained, Franck-Condon factors can be evaluated by integrating numerically the equation 1 using Numerov Method as given in Leroy's program[13]. The results are compiled in Table 2 to Table 4.

## III. EXPERIMENTAL BACKGROUND

The laboratory experiment have yielded several singlet and triplet transitions in  $S_2$  in the VUV region (160 nm to 130nm). The analysis of these transitions, both vibrational as well as rotational have led to the identification of several Rydberg transitions. For example, E-X is a  $n=5$  Rydberg member of  $(\pi_g 3p)(\pi_u np)$  that converges to the lower spin component of the ground state  $^2\Pi_{1/2}$  of  $S_2^+$  and H & I constitute another Rydberg series  $(\pi_u 3p)^3(\pi_g 3p)^2(n\sigma_g)$  that converges to  $^4\Pi_{1/2}$  of  $S_2^+$  [15,16]. The progressions comprising these Rydberg transitions are small but the detailed rotational analysis help us to provide the necessary required data for the present work.

## Dissociation energy and potential energy curves of E, H and I states

Using the universal relation between spectroscopic constants  $G(=8\omega_e x_e/6B_e^2)$  and the

Sutherland parameter  $\Delta(=k_e r_e^2/2D_e)$  [9] i.e.

$\ln G = 91578 (\pm 0.09727) + 0.97111 (\pm 0.03809) \ln \Delta$  with correlation coefficient as 0.97 or  $\ln \Delta = 1.02975 \ln G - 1.97277(2)$  (without standard deviation) dissociation energy of E, H and I electronic state is calculated to be 14873, 2795 and  $8418 \text{ cm}^{-1}$  respectively. Using this  $D_e$  value supplemented with the experimental data for  $\omega_e$ ,  $r_e$  and the analytical potential function  $U_1$ [9], the vibronic states and hence the bands expected from the transitions among these states have been obtained numerically employing the fourth order Runge-Kutta method. The agreement between the calculated and the experimental values reinforce our earlier findings on  $X \Sigma_g^+$ ,  $a^1 \Delta_g$ ,  $b^1 \Sigma_g^+$  electronic states of  $S_2$ [9] that the Universal relation provide the heat of dissociation of various electronic states of  $S_2$  that are close to the actual values.

## IV. RESULTS AND DISCUSSIONS

Meyer and Crosley[10] obtained the FC factors  $q_{3v'}$  and  $q_{4v'}$  from the  $B^3E_u'$  state to the ground state  $X^3\Sigma_g^-$  state of  $S_2$ , using selective excitation of resonance fluorescence. Their intensity values, as suggested by them are taken as reliable and inexpensive intensity standards. Table 2 contains our results. The table also include the values of Meyer and Crosley[10], Morse potential based values of Herman and Felenbole [11] and RKR based values of Me Callum et al[12] for comparison. Our results agree qualitatively with the estimated intensity values of Meyer and Crosley. The discrepancies are very possibly because the Morse potential may not represent the true potential, as is usually the case for the higher vibrational levels, of the electronic states involved in the transitions. Similar is the case with FC factor for C-X transitions as is evident from the Table 3. The Values agree qualitatively with the experimental intensities given by Tanaka and Ogawa[19]. The FC factors for E-X, H-X and I-X transitions are comprised in Table 4. Since the change in internuclear distance in E [ $0.18912 (r_e'') - 0.1839 (r_e') = 0.0052 \text{ nm}$ ] decrease and I [ $0.19446 (r_e') - 0.18912 (r_e'') = 0.00534 \text{ nm}$ ] are nearly same in magnitude, the intensity distribution in E-X & I-X are expected to be similar and also, since the change is very small, the first band is expected to be very intense. Our FC factors values are in consonance with these experimental observations. While, the change in internuclear distance [ $0.19973 (r_e') - 0.18912 (r_e'') = 0.01061 \text{ nm}$ ] in state H is roughly twice that in state E or I, (0,0) band in H-X may not therefore, be most intense, though not weak also. FC factors are in consistence with these observations. Furthermore, if sum rule is to be satisfied, few more bands are expected to be

observed, particularly the bands (4,0) and (5,0) in H-X and (3,0), (4,0) and (5,0) in I-X. Assuming our vibrational assignments, as reinforced by the present FC factor calculations, in the electronic transitions E-X, H-X and I-X to be correct, the dissociation energy of electronic states E, H and I are calculated to be 14873, 2794 and 8418  $\text{cm}^4$ , respectively. These values together with the vibrational data of X, E, H and I electronic states [9,15,16,19], lead to the minima of potential curves of E, H and I at 65830, 66520 and 68334  $\text{cm}^{-1}$  w.r.t the equilibrium minimum of  $X^3\Sigma_g^-$ . These values when taken with the energy of  $^1S$ ,  $^1D$  atomic states of SI from Grotarian diagram, state E is expected to dissociate into  $^1S+^1S$  [ $65830 + 14873 - 36556 = 44147 \text{ cm}^{-1}$ ] and so is the case with the state I [ $68334 + 8418 - 36556 = 40196 \text{ cm}^4$ ] (Fig. 1). On the other hand, state H dissociate into  $^1S+^1D$  [ $66520 + 2794 - 36556 = 32758 \text{ cm}^4$ ]. However, state E is  $1_u$  (under  $\Omega_c$ ,  $\omega$  coupling) i.e.  $e\Omega = 1$  [15,16] and  $^1S+^1S$ , under Hund's case 'c', yield  $\Omega = 0$ . Therefore, state E would not dissociate into  $^1S+^1S$ . However, in view of the complexity of several Rydberg states having same  $\Omega$  values [15,16], very possibly the potential curve of E goes, to avoid crossing of potential curves of same species, over to  $^1S+^1D$  which has  $\Omega=2,1$  and 0 values. Work is under progress for its confirmation.

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Table 1. Experimental constants for different electronic states of S2 Molecule to calculate FC Factor

S. No.	Molecular State	$r_e(\text{Å})$	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$D_e = \omega_e^2 / 4\omega_e x_e(\text{cm}^{-1})$
1.	$X^3\Sigma_g^-$	1.8892	725.65	2.844	46290
2.	$B^3\Sigma_u^-$	2.1700	434.00	2.750	17123
3.	$C^3\Sigma_u^-$	1.7820	829.15	3.344	51458
4.	$E O_u^+$	1.8470	817.23	8.590	19439
5.	$HOu^+$	1.9850	662.30	28.800	3804
6.	$IOu^+$	1.9446	606.30	8.325	11039

Table 2. Comparison of FC factors for B-X system.

$v''$	$q_{3,v''}$				$q_{4,v''}$			
	Present Work	Expt. [Ref. 10]	Ref [11]	Ref [12]	Present Work	Expt. [Ref. 10]	Ref [11]	Ref [12]
0	0.00364	0.0040	0.001	0.001	0.0083	0.0090	0.0040	0.0030
1	0.022	0.0210	0.012	0.011	0.0410	0.0390	0.0230	0.0220
2	0.062	0.0670	0.0390	0.0380	0.0799	0.0820	0.0600	0.0590
3	0.088	0.100	0.0740	0.0740	0.0693	0.0690	0.0790	0.0790
4	0.0640	0.0720	0.0810	0.0810	0.0160	0.0110	0.0460	0.0470
5	0.0130	0.0060	0.0420	0.0430	0.0045	0.0110	0.0030	0.0030
6	0.0026	0.0170	0.0030	0.0030	0.0452	0.0610	0.0150	0.0150
7	0.0450	0.0670	0.0140	0.0140	0.0503	0.0540	0.0520	0.0520
8	0.0620	0.0690	0.0520	0.0530	0.0080	0.0050	0.0390	0.0390
9	0.0250	0.0200	0.0550	0.0540	0.0097	0.0160	0.0030	0.0030
10	0.0034	0.0030	0.0170	0.0160	0.0520	0.0620	0.0140	0.0150
11	0.0360	0.0480	0.0010	-----	0.0440	0.0460	0.0490	-----
12	0.0714	0.0760	0.0160	-----	0.0029	0.0030	0.0020	-----

Table 3. FC factors for C-X transition

$v',v''$	FC Factor	Intensity (ref. 19)
0,0	0.1299	3
0,1	0.1239	
0,2	0.2398	3
0,3	0.1780	3
0,4	0.1086	1
0,5	0.0577	1
0,6	0.0277	0
0,7	0.0123	
0,8	0.0052	
0,9	0.0021	

Table 4: Calculated FC factors of E, H and I-X transitions

FC factor for E-X		FC factor for H-X		FC factor for I-X	
$v',v''$	$q_{v',v''}$	$v',v''$	$q_{v',v''}$	$v',v''$	$q_{v',v''}$
0,0	0.6963	0,0	0.1674	0,0	0.6034
1,0	0.2631	1,0	0.1867	1,0	0.2544
2,0	0.0387	2,0	0.1495	2,0	0.0874
3,0	0.0018	3,0	0.1087	3,0	0.0316
		4,0	0.0769	4,0	0.0126
		5,0	0.0539	5,0	0.0054

Table 5. Molecular constants for Potential energy curves of different electronic states of S2

Sr. No.	Molecular state	$r_e$ (Å°)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$D_e^*$ (cm <sup>-1</sup> )	$T_e$ (cm <sup>-1</sup> )
1.	X <sup>3</sup> Σ <sub>g</sub> <sup>-</sup>	1.8892	725.65	2.844	36556	-----
2.	E O <sub>2</sub> <sup>+</sup>	1.8470	817.23	8.590	14873	65830
3.	H O <sub>2</sub> <sup>+</sup>	1.9850	662.30	28.800	2795	66520
4.	IO <sub>2</sub> <sup>+</sup>	1.9446	606.30	8.325	8418	68334

\* Dissociation energy values are taken from ref.9 and ref. 18.

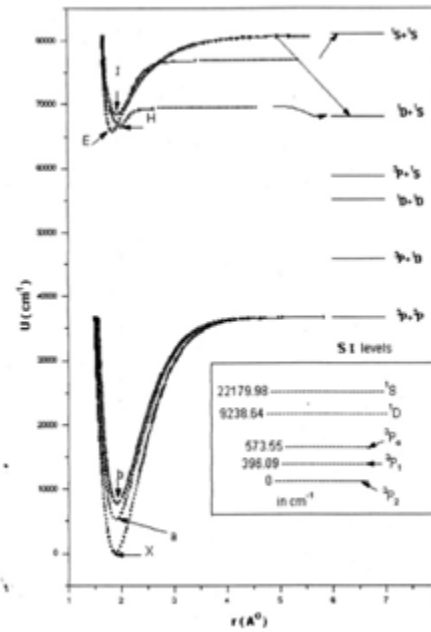


Fig 1