ISSN 0974 - 9373

Vol. 14 No.2 (2010) **Journal of International Academy of Physical Sciences** pp. 233-243

Laser Produced Spectra of SiC Molecule in the Region of 550-1020 nm*

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(Received February 20, 2010)

Abstract: Emission spectra of SiC molecule, consisting of about 160 bands, are recorded in the region 550-1020 nm using laser ablation technique. Out of total 160 bands, 140 bands are analyzed into 4 new band systems along with one previously reported. Molecular constants of all the systems are reported.

Key words: Emission spectra, SiC molecule, LIBS of SiC, molecular constants.

1. Introduction

SiC molecule is found in carbon stars, steller atmospheres and in the interstellar molecular clouds. Thus like other silicon bearing molecules, SiC is of astrophysical importance. Lutz and Ryan[1] on the basis of CI calculations for SiC molecule reported three electronic states $^3\Pi$, $^3\Sigma^-$ and $^1\Sigma^+$ and showed that the $^3\Pi$ is ground state with ω_e=983 cm^{-1}. Bruna *et al.*[2] reported large-scale ab-initio CI calculations for the potential curves of the SiC and calculated five low lying electronic states $^3\Pi$ ($\pi^3\sigma$), $^3\Sigma^-$ ($\pi^2\sigma^2$), $^1\Pi$ ($\pi^3\sigma$), $^1\Sigma^+$ (π^4) and $^1\Delta$ ($\pi^2\sigma^2$) with their T_e, r_e and ω_e values. Rohlfing and Martin[3] performed ab-initio calculation considering of electron correlation effect on $^3\Pi$ state of SiC molecule and determined the equilibrium geometries and spectroscopic constants for this state. Larsson[4] using CASSCF and contracted CI methods calculated the potential curves of $X^3\Pi$, $B^3\Sigma^+$ and $C^3\Pi$ states for SiC molecule and predicted that the transitions B-X and C-X would fall in the region of 600-400 nm. He also reported the molecular constants of $X^3\Pi$, $B^3\Sigma^+$ and $C^3\Pi$ states and the Frank-Condon factors for the $C^3\Pi$-$X^3\Pi$ and $B^3\Sigma^+$-$X^3\Pi$ transitions. Bauschlicher and Langhoff[5] performed full configuration-interaction (FCI) calculations for the $X^3\Pi$ and $A^3\Sigma^-$ states of SiC molecule and reported the modified spectroscopic constants for these two states.

*Presented at CONIAPS XI, University of Allahabad, Feb. 20-22, 2010.

Bernath *et al.*[6] first observed the (0,0) band of $d^1\Sigma^+$-$b^1\Pi$ system of the SiC molecule in microwave region by high resolution Fourier-transform emission spectroscopy using composite-wall hollow cathode and theoretically calculated six low-lying electronic states $X^3\Pi$, $A^3\Sigma^-$, $a^1\Sigma^+$, $b^1\Pi$, $c^1\Delta$ and $d^1\Sigma^+$ states. Cernicharo *et al.*[7] observed a number of millimeter-wave rotational lines of $X^3\Pi$ ground state and determined the rotational, centrifugal distortion and Λ-doubling constants of SiC molecule. Brazier *et al.*[8] studied two bands (0,0) and (0,1) of $A^3\Sigma^-$-$X^3\Pi$ system in microwave region using the high resolution Fourier-transform spectroscopy. Langhoff *et al.*[9] made a theoretical study of $A^3\Sigma^-$-$X^3\Pi$ infrared transition of SiC using atomic natural orbital Gaussion basis sets in conjunction with multireference configuration interaction calculation and proposed the value of T_{00} = 3700 ± 200 cm^{-1}. They reassigned the (0,0) band reported by Brazier *et al.*[8] as (1,0) band of $A^3\Sigma^-$-$X^3\Pi$ system. Martin *et al.*[10] reported modified spectroscopic constants of the three low-lying electronic states $X^3\Pi$, $A^3\Sigma^-$ and $a^1\Sigma^+$ of SiC molecule using augmented coupled cluster methods and different basis set.

Ebben *et al.*[11] observed seven bands of $C^3\Pi$-$X^3\Pi$ system of SiC molecule in the region of 442-384 nm using laser vaporization technique in combination with supersonic cooling and the transitions are detected using pulsed LIF spectroscopy and modified the vibrational and rotational constants of the $C^3\Pi$ (ω_e = 618.85 cm^{-1}) and $X^3\Pi$ (ω_e = 964.60 cm^{-1}) states. Butenhoff *et al.*[12] reported LIF spectroscopic investigation of $C^3\Pi$-$X^3\Pi$ band system of SiC molecule and observed nine bands including seven bands reported by Ebben *et al.*[11] They modified vibrational constants of $C^3\Pi$-$X^3\Pi$ transition with T_e = 22829.40 cm^{-1}, ω_e' = 615.72 cm^{-1} and ω_e'' = 965.15 cm^{-1}. Grutter *et al.*[13] observed three band systems $A^3\Sigma^-$-$X^3\Pi$, $B^3\Sigma^+$-$X^3\Pi$ and $C^3\Pi$-$X^3\Pi$ in 5 K neon matrices in absorption (0,0) lying at 2675.22 nm, 851.10 nm and 440.70 nm respectively along with two new band systems of SiC^-. Recently, Deo *et al.*[14] observed gas phase infrared emission spectrum of the $A^3\Sigma^-$-$X^3\Pi$ electronic transition of SiC using high resolution Fourier transform spectroscopy and reported three bands (0,1), (0,0) and (1,0) lying at 3610.10 nm, 2686.00 nm and 2184.35 nm respectively. On the basis of rotational analysis of these bands, they modified the molecular constants.

From the above concerned literatures, it is clear that the available data about SiC molecule in visible and near IR regions are insufficient. The laser ablation technique is being widely used in the field of molecular spectroscopy to provide laboratory data of elusive molecules. Bondebey[15],

Smelly *et al.*[16] and Ojha and Gopal[17] have observed a number of new band systems of different molecules using this technique. Therefore, it is decided to record the spectra of SiC molecule in the region of 1020 – 550 nm.

2. Experimental Technique

The experimental arrangement is shown in Figure 1. It consists of a pulsed Nd: YAG Laser (Spectra Physics, USA), 10″ diameter cylindrical ablation chamber mounted on the throat of rotary and diffusion pumps and a computer controlled Spex TRIAX 320 M monochromator (Jobin Yovn, USA) fitted with TE cooled ICCD detector system (Jobin Yovn, USA).

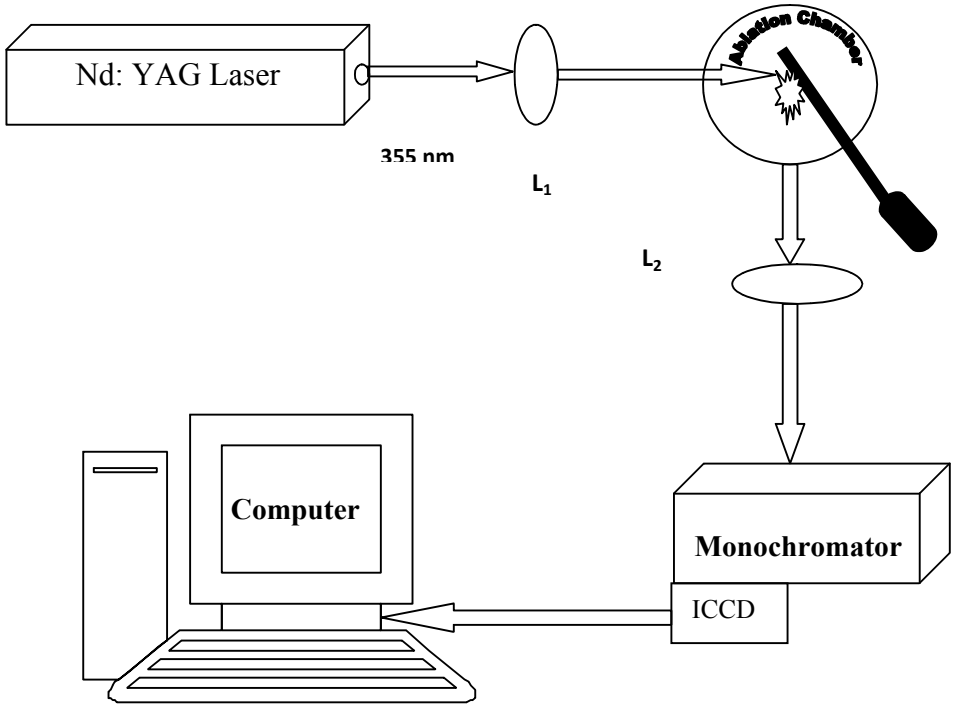

Figure 1. Experimental Setup

The laser ablation chamber is evacuated up to 10^{-3} torr using rotary pump. The chamber is flushed with argon gas two to three times to remove the impurity and finally evacuated. The chamber is filled with high purity argon gas as an ambient atmosphere of 10^{-1} torr. The SiC rod (99.999%, Goodfellow, UK) is used as a target. 170 mJ energy of third harmonic (355 nm) of Pulsed Nd: YAG laser is focused on a rotating and translating target inside the ablation chamber using a convex lens of focal length 50 cm. The adiabatic cooling of the produced plasma is allowed for some time and the

Spex TRIAX 320 M monochromator fitted with TE cooled ICCD detector system is used to collect the radiation from the cooled plasma. The radiation is collected on the entrance slit of monochromator using a cylindrical lens of 25 cm. The signals from ICCD are sent to the computer and data acquisition is made using Spectra Max software while Grams 32 software is used for peak marking and peak picking. The spectra of SiC molecule are recorded at pressure of 10^{-1} torr and at different delay times starting from 100-600 ns with 5 accumulations in gated mode of ICCD. The reported bands of SiC molecule are appeared at 320 ns delay time. The spectra of SiC molecule are recorded 550-1020 nm with 600 grs/mm grating blazed at 750 nm.

3. Result and Analysis

The spectra of SiC molecule recorded in the region of 550-1020 nm consist of about 160 bands. Out of total 160 bands, about 142 bands are assigned to 4 new band systems along with one reported by Grutter *et al.*[13]. The system wise analyses of these bands are as given below.

3.1. $B^3\Sigma^+$-$X^3\Pi$ System:

The B-X system lies in the region of 620-1017 nm with (0,0) at 851.30 nm. The total 25 violet degraded and single headed bands of this system are identified and analyzed into $\Delta v = 0, \pm 1, \pm 2, + 3$ and $+ 4$ sequences including all the four bands reported by Grutter *et al.*[13] The bands of $\Delta v = 0$ sequence are observed with low signal to noise ratios while the bands of other sequences are observed with good intensity. The new head position for (1,0) and (2,0) bands has been found to be shifted towards red from the data reported by Grutter *et al.*[13] The molecular constants of $B^3\Sigma^+$ are in close agreement to that reported by earlier worker. The bandhead data of this system are given in Table 1 and the spectra are displayed in Figures 2, 3, 4 and 5. The molecular constants of $B\,^3\Sigma^+$ and $X^3\Pi$ states are as follows;

$\upsilon_e = 11657.36\ cm^{-1}$

$\omega_e' = 1140.0\ cm^{-1}$	$\omega_e'x_e' = 7.50\ cm^{-1}$	$\omega_e'y_e' = -0.26\ cm^{-1}$
$\omega_e'' = 965.20\ cm^{-1}$	$\omega_e''x_e'' = 5.95\ cm^{-1}$	$\omega_e''y_e'' = 0.58\ cm^{-1}$

3.2. New C´-A System:

The system lies in the region of 554-1012 nm with (0,0) at 918.66 nm. About 29 violet degraded and single headed bands are attributed to this system. All these bands are well developed and analyzed into $\Delta v = 0, \pm 1, \pm 2, \pm 3$ and $+ 4$ sequences. The bandhead data of C-$A^3\Sigma^-$ system are given in Table 2. The spectra are displayed in Figures 2, 3, 4 and 5. The vibrational constants of lower state $A^3\Sigma^-$ are the same as reported by Deo *et al.*[14]. The vibrational constants of both the states are as follows;

υ_e= 10563.68 cm^{-1}
ω_e' = 1500.00 cm^{-1} $\omega_e'x_e'$ = 6.50 cm^{-1} $\omega_e'y_e'$ = 0.23 cm^{-1}
ω_e'' = 862.20 cm^{-1} $\omega_e''x_e''$ = 4.92 cm^{-1} $\omega_e''y_e''$ = -0.25 cm^{-1}

3.3. New D-A system:

The D-$A^3\Sigma^-$ system consists of about 31 red degraded and single headed bands. The system lies in the region of 685-1018 nm with (0,0) at 892.86 nm. All the 31 bands are analyzed into $\Delta v = 0, \pm 1, + 2, + 3, + 4$ and + 5 sequences. The bands of $\Delta v = 0$ and ± 1 sequences are well developed. The bands of $\Delta v = + 2, + 3, + 4$ and + 5 sequences are relatively weaker. The bandhead data of this system are given in Table 3 and spectra are displayed in Figures 3, 4 and 5. The vibrational constants for state $A^3\Sigma^-$ are same as reported by Deo *et al.*[14]. The molecular states for both the states are given below;

υ_e= 11270.45 cm^{-1}
ω_e' = 715.00 cm^{-1} $\omega_e'x_e'$ = 5.00 cm^{-1} $\omega_e'y_e'$ =- 0.14 cm^{-1}
ω_e'' = 862.20 cm^{-1} $\omega_e''x_e''$ = 4.92 cm^{-1} $\omega_e''y_e''$ =-0.25 cm^{-1}

3.4. New E-A system:

The E-$A^3\Sigma^-$ system lies in the region of 639-1000 nm with (0,0) at 857.32 nm. It consists of about 23 violet degraded and single headed bands. All these bands are analyzed into $\Delta v = 0, \pm 1, \pm 2, + 3$ and + 4 sequences. The (0,0) band is the most intense incomprasion to the other sequences. The bandhead data of this system are given in Table 4. The spectra of this system are presented in Figures 2, 3, 4 and 5. The vibrational constants of E-$A^3\Sigma^-$ system are as follows;

υ_e= 11591.07 cm^{-1}
ω_e' = 1006.0 cm^{-1} $\omega_e'x_e'$ = 9.20 cm^{-1} $\omega_e'y_e'$ =0.09 cm^{-1}
ω_e'' = 862.2 cm^{-1} $\omega_e''x_e''$ = 4.92 cm^{-1} $\omega_e''y_e''$ =-0.25 cm^{-1}

3.5. New F-A system:

The system lies in the region of 565-1010 nm and about 34 violet degraded and single headed bands of this system are identified. The (0,0) band of this system lies at 828.18 nm. All the 34 bands are analyzed into $\Delta v = 0, \pm 1, \pm 2, \pm 3, + 4$ and + 5 sequences. The bands of $\Delta v = 0, - 1, \pm 2, \pm 3$ and + 4 sequences are well developed and observed with good intensity. The bands of $\Delta v = + 1, + 2$ and + 5 sequences are weak. The bandhead data of F-$A^3\Sigma^-$ system are given in Table 5. The spectra of this system are presented in Figures 2, 3, 4 and 5. The vibrational constants of F-$A^3\Sigma^-$ system are as given below;

υ_e= 11914.66 cm^{-1}

$\omega_e' = 1173.0\ cm^{-1}$ $\omega_e'x_e' = 8.00\ cm^{-1}$ $\omega_e'y_e' = -0.13\ cm^{-1}$
$\omega_e'' = 862.2\ cm^{-1}$ $\omega_e''x_e'' = 4.92\ cm^{-1}$ $\omega_e''y_e'' = -0.25\ cm^{-1}$

Table 1. Bandhead Data of B-X System

v′, v″	λ (nm, air)	*v* (vacuum)	v′, v″	λ (nm, air)	*v* (vacuum)
4,0	620.08	16122.42	4,4	810.45	12335.36
6,3	653.43	15299.56	3,3	818.78	12209.86
5,2[+]	656.60	15225.70	2,2	827.31	12083.97
4,1	659.34	15162.42	1,1	839.59	11907.23
3,0	663.53	15066.67	0,0[+]	851.30	11743.44
6,4	692.94	14427.21	2,3	896.84	11147.13
5,3	696.70	14349.35	1,2	909.34	10993.90
4,2	701.58	14249.54	0,1	925.40	10803.10
2,0[+]	713.38	14013.83	4,6	958.25	10432.76
3,2	758.77	13175.52	2,4	980.03	10201.21
1,0[+]	776.74	12870.70	1,3	997.38	10023.45
6,6	800.18	12493.68	0,2	1016.60	9833.95
5,5	804.90	12420.41			

[+] Bands reported by Grutter *et al.*[13]

Table 2. Bandhead Data of C'-A System

v′, v″	λ (nm, air)	*v* (vacuum)	v′, v″	λ (nm, air)	*v* (vacuum)
6,2	554.79	18019.77	7,7	647.84	15431.57
5,1	574.82	17391.86	6,6	677.99	14745.33
4,0*	596.18	16768.74	5,5*	707.89	14122.52
7,4	563.66	17736.20	3,3	780.46	12809.35
6,3	581.40	17195.03	2,2	822.01	12161.88
5,2	602.49	16593.12	1,1	871.38	11472.82
4,1	628.08	15917.06	0,0	918.66	10882.36
3,0	655.38	15254.03	2,3	882.61	11326.85
5,3	635.83	15723.05	1,2	934.49	10698.02
4,2	667.53	14976.40	0,1	993.89	10058.65
3,1	689.86	14491.62	3,5	894.99	11170.17
2,0	728.76	13718.08	2,4	949.79	10525.68
4,3	703.97	14201.16	1,3	1012.20	9876.70
3,2	733.90	13622.00	3,6	960.55	10407.78
1,0	807.97	12373.22			

*Bands overlapped by atomic lines

Table 3. Bandhead Data of D-A System

v′, v″	λ (nm, air)	*v* (vacuum)	v′, v″	λ (nm, air)	*v* (vacuum)

8,3	715.77	13967.04	3,2	862.71	11588.12
7,2*	705.83	14163.74	2,1	852.89	11721.55
6,1	694.47	14395.42	1,0	839.95	11902.12
5,0	685.83	14576.77	6,6	966.75	10341.03
7,3	749.99	13329.76	5,5	954.76	10470.89
6,2	737.89	13548.35	4,4	940.90	10625.13
5,1	726.39	13762.84	3,3	929.91	10750.71
4,0	717.83	13926.96	2,2	917.31	10898.38
7,4	797.48	12535.97	1,1	904.89	11047.96
6,3	785.09	12733.81	0,0	892.86	11196.82
5,2	774.18	12913.26	4,5	1018.40	9816.56
8,6	864.69	11561.59	3,4	1004.20	9955.38
7,5	852.04	11733.24	2,3	993.18	10065.84
4,2	815.48	12259.27	1,2	978.13	10220.72
3,1	805.74	12407.46	0,1	963.24	10378.71
2,0	793.65	12596.47			

* Band overlapped by atomic line.

Table 4. Bandhead Data of E-A System

v′, v″	λ (nm, air)	*v* (vacuum)	v′, v″	λ (nm, air)	*v* (vacuum)
6,2	639.26	15638.69	2,1	782.14	12781.84
5,1	643.86	15526.96	1,0	788.63	12676.65
4,0	650.71	15363.51	5,5	813.11	12295.00
6,3	673.82	14836.59	2,2*	833.98	11987.32
5,2	676.88	14769.51	0,0	857.32	11660.98
4,1	680.68	14687.06	0,1	924.51	10813.50
3,0	683.99	14616.00	4,6	945.27	10576.01
5,3	719.41	13896.37	3,5	957.32	10442.89
4,2	723.90	13810.18	2,4	969.48	10311.91
3,1	729.02	13713.20	1,3	985.62	10143.05
2,0	734.14	13617.55	0,2	1000.20	9995.20
6,5	757.07	13205.11			

* Band overlapped by atomic line.

Table 5. Bandhead Data of F-A System

v′, v″	λ (nm, air)	*v* (vacuum)	v′, v″	λ (nm, air)	*v* (vacuum)

5,0	565.56	17676.62	3,3	771.71	12954.60
8,4	570.59	17520.80	2,2	790.34	12649.23
7,3	578.08	17293.78	1,1	808.00	12372.76
6,2	588.02	17001.44	0,0	828.18	12071.28
4,0	604.40	16540.68	4,5	800.73	12485.10
8,5	599.37	16679.50	3,4	821.90	12163.51
7,4	606.30	16488.85	1,2	869.39	11499.08
5,2	626.37	15960.52	0,1	891.31	11216.29
4,1	634.16	15764.46	5,7	832.31	12011.38
3,0	645.72	15482.24	4,6	854.74	11696.18
5,3	661.6	15110.62	3,5	881.34	11343.17
4,2	670.73	14904.94	1,3	933.25	10712.23
3,1	687.20	14547.71	0,2	965.25	10357.10
2,0	699.07	14300.70	4,7	915.47	10920.28
4,3	711.31	14054.62	3,6	943.80	10592.49
3,2	725.65	13776.87	2,5	975.44	10248.90
5,5	736.04	13582.40	1,4	1009.40	9904.09

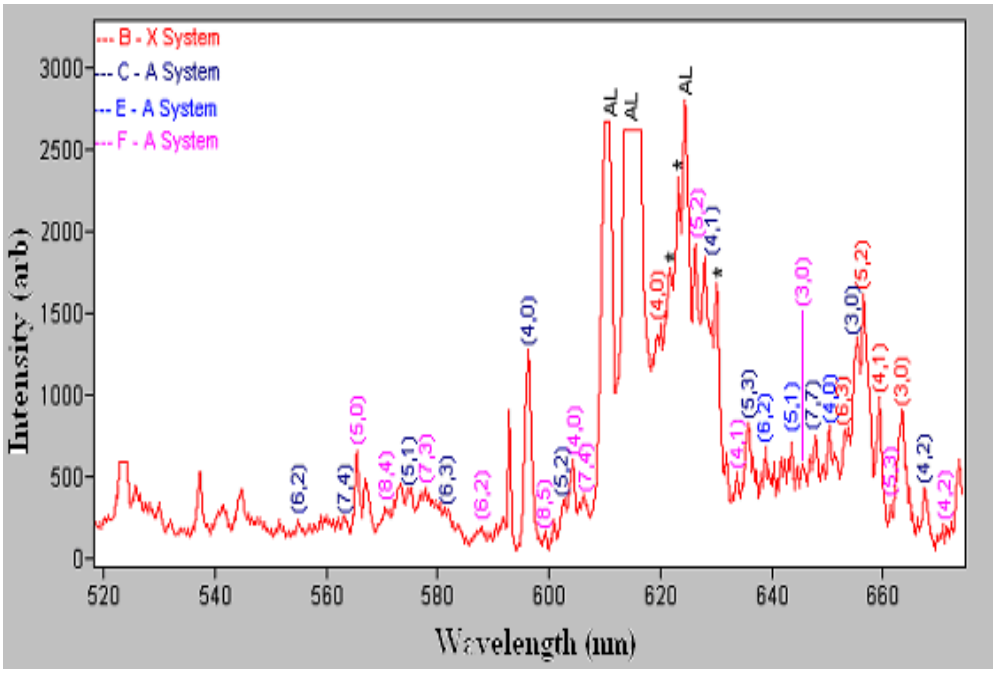

Figure 2. Laser Produced Spectrum of SiC Molecule

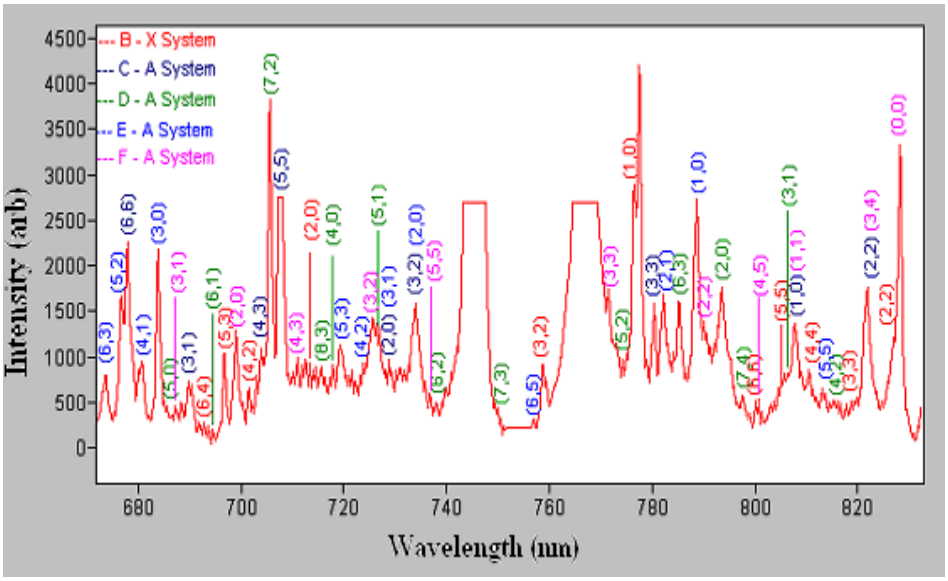

Figure 3. Laser Produced Spectrum of SiC Molecule

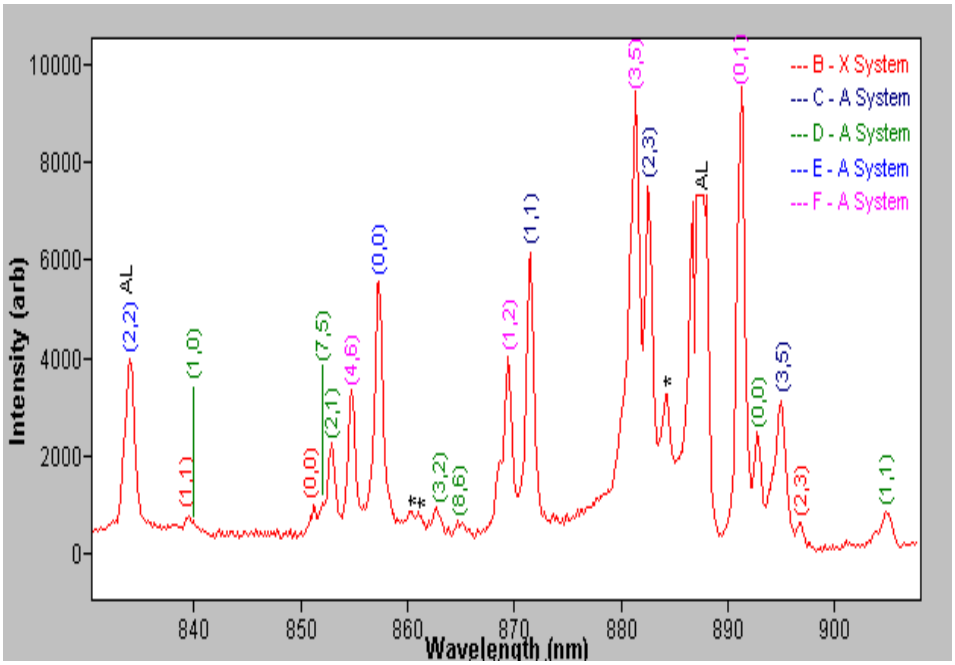

Figure 4. Laser Produced Spectrum of SiC Molecule

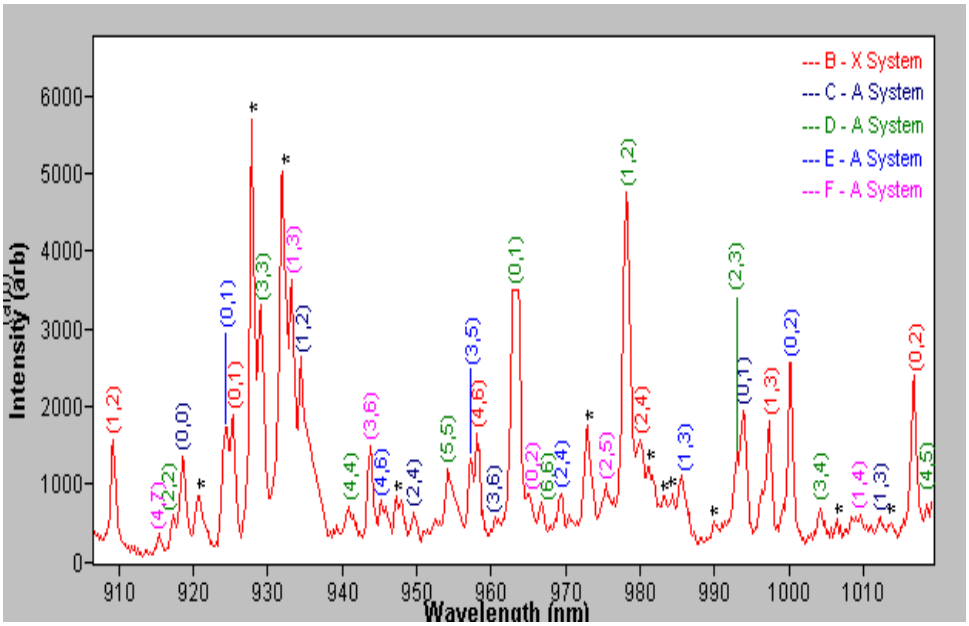

Figure 5. Laser Produced Spectrum of SiC Molecule

4. Discussion

The molecular constants for $X^3\Pi$ and $A^3\Sigma^-$ states are very close to that reported by Butenhoff *et al.*[12] and Deo *et al.*[14] The number of electrons in SiC molecule is 20, which are even. Therefore the term values that take place in transition are of odd multiplicities. The ground state electronic configuration of Si and C are given as;

$_{14}Si = K\ L\ 3s^2\ 3p^2$ $_{6}C = K\ 2s^2\ 2p^2$

The outermost four valance electrons of silicon and four valance electrons of carbon are responsible for the formation of SiC molecule. These eight valance electrons are distributed in the following manner giving rise to the some low-lying electronic states of SiC molecule;

$K\ K\ L\ (z\sigma)^2\ (y\sigma)^2\ (w\pi)^3\ (x\sigma)$ ----------$^3\Pi, {}^1\Pi$

$\pi^2\ \sigma^2$ ----------$^3\Sigma^-, {}^1\Sigma^+, {}^1\Delta$

π^4 ----------$^1\Sigma^+$

$\pi^2\ \sigma\ \pi$ ----------$^1\Pi, {}^1\Phi, {}^3\Pi_r, {}^3\Pi_i$

On the basis of rotational studies, earlier workers Brazier *et al.*[8], Butenhoff *et al.*[12], Ebben *et al.*[11], Grutter *et al.*[13] and Deo *et al.*[14] have shown that the ground state of SiC molecule is $^3\Pi$ state arises from $\pi^3\sigma$ while the next excited state is $A^3\Sigma^-$ ($\pi^2\ \sigma^2$). Bruna *et al.*[2], Larsson[4], Bernath *et al.*[6] and Martin *et al.*[3], on the basis of theoretical calculation, showed that

the $X^3\Pi$ arises from $\pi^3\sigma$, $A^3\Sigma^-$ state from $\pi^2\sigma^2$, $a^1\Sigma^+$ from π^4, $b^1\Pi$ from $\pi^3\sigma$, $c^1\Delta$ and $d^1\Sigma^+$ from $\pi^2\sigma^2$ configurations respectively.

References

1. B. L. Lutz and J. A. Ryan, *Astrophys. J.*, **194** (1974) 753.
2. P. J. Bruna, S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **72** (1980) 5437.
3. C. Rohlfing and Martin, *J. Phys. Chem.*, (1986).
4. Mats Larsson, *J. Phys. B: At. Mol. Phys.*, **19** (1986) L261.
5. C. W. Bauschlicher Jr. and Stephen R. Langhoff, *J. Chem. Phys.*, **87** (1987) 2919.
6. P. F. Bernath, S. A. Rogers, L. C. O'Brien and C. R. Brazier, *Phys. Rev. Lett.*, **60**, (1988) 197.
7. J. Cernicharo, C. A. Gottlieb, M. Guelin, P. Thaddeus and J. M. Vrtilek, *Astrophys. J. Lett.*, **341** (1989) L 25.
8. C. Brazier, L. C. O'Brien and P. F. Bernath, *J. Chem. Phys.*, **91** (1989) 7384.
9. S. R. Langhoff and C. W. Bauschlicher,Jr, *J. Chem. Phys.*, **93** (1990) 42.
10. J. M. L. Martin, J. P. Fracois and R. Gijbels, *J. Chem. Phys.*, **92** (1990) 6655.
11. M. Ebben, M. Drabbels and J. J. ter Meulen, *J. Chem. Phys.*, **95 (4)** (1991) 2292.
12. T. J. Butenhoff and E. A. Rohlfing, *J. Chem. Phys.*, **95 (6)** (1991) 3939.
13. M. Grutter, P. Freivogel and J. P. Maier, *J. Phys. Chem. A*, **101** (1997) 275.
14. M. N. Deo and K. Kawaguchi, *J. Mol. Spectroscopy*, **76** (2004) 228.
15. V. E. Bondybey, *J. Phys. Chem.*, **86** (1982) 3396.
16. D. L. Michalopoulos, M.E.Geusic, P.R.R. Langridge- Smith, R.E. Smalley, *J. Chem. Phys.*, **80** (1984) 3556.
17. K. S. Ojha and R. Gopal, *Indian J. of Phys.*, **80(8)** (2006) 819.