

Reinvestigation of Emission Spectra of Silicon Dimer in 360-540 nm Region

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Abstract : The emission spectra of silicon dimer were reinvestigated in the region of 360-540 nm using laser ablation technique. About 100 bands were observed in this region and all these bands were classified into three transitions. Out of these three transitions, two transitions in 454-538 nm and 360-415 nm regions were new while the third transition, in 362-470 nm region, had been previously reported as H-X transition. The molecular constants of all these three transitions were determined and reported.

Keywords: Silicon dimer, LIBS of Si₂ molecule, electronic transition, molecular constants.

1. Introduction

Silicon is the most depleted abundant element representing a major constituent of interstellar dust grains ¹ and Jones ² concluded from the analysis of depletion patterns and dust processes in different regions of the diffuse interstellar medium (ISM) that Si is more easily eroded from dust than any of the other elements. Out of the large number of gas-phase astronomical molecules, a good number of molecules containing silicon have been identified. Thus silicon and silicon bearing molecules are of astrophysical importance. The two band systems of Si₂ molecule, laying in the region 348-430 nm, were observed by Douglas ³ in electric discharge and assigned as $L^3\Pi_g \leftarrow D^3\Pi_u$ and $H^3\Sigma_u \leftarrow X^3\Sigma_g$ -transitions. In addition to $H^3\Sigma_u \leftarrow X^3\Sigma$ transition, Verma and Warsop ⁴ had observed two new

systems $N^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ and $K^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$, with band origins at 210 nm and 320 nm respectively, in absorption using flash photolysis. Redondo *et al.*⁵ and Weinert *et al.*⁶, on the basis of CI and LSD calculations, showed that the ground state of silicon dimer would be $H^3\Sigma_u^-(\sigma_g^2\pi_u^2)$. Lagerquist and Malmberg⁷ had observed two new systems $O^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ and $P^3\Pi_g \leftarrow D^3\Pi_u$ along with $N^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ systems reported by Verma and Warsop⁴. A new $D^3\Pi_u \leftarrow X^3\Sigma_g^-$ band system was observed by Milllingan and Jacox⁸ in the region 270-290 nm. Dubious and Lecqure⁹⁻¹⁰ reported a new singlet-singlet system along with already reported $L^3\Pi_g \leftarrow D^3\Pi_u$, $H^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ and $K^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ systems. Bruna *et al.*¹¹ theoretically predicted potential energy curves for the low-lying states of isovalent diatomic CN^+ , Si_2 , SiC , CP^+ and SiN^+ using the ab-initio MRD-CI method and found that the system assigned as $D^3\Pi_u \leftarrow X^3\Sigma_g^-$ by Milllingan and Jacox⁸ was not correct. Similar observations had been later on made by Ellison *et al.*¹² and Kitsopoulos *et al.*¹³. Davis and Brault¹⁴ observed first emission spectra of Si_2 dimer and assigned it as $d^1\Sigma_g^+ \rightarrow b^1\Pi_u$ transition with band origin at 2253.5 nm. Electronic absorption spectra of silicon clusters Si_n and Si_n^- ($n = 2-4$) had been observed by Fulara *et al.*¹⁵ in 5⁰K neon matrices using mass selection and code position technique and tentatively reported H-X system of Si_2 molecule. From the above concerned literatures, it is clear that the available data of silicon dimer are insufficient and inconsistent. Morse *et al.*¹⁶ Smelly *et al.*¹⁷ and Ojha and Gopal¹⁸⁻¹⁹ and Singh *et al.*²⁰, using the laser induced plasma spectroscopy techniques, had been observed a good number of new bands of different molecules using this technique. Therefore, it was decided to reinvestigate the spectra of silicon dimer in the region of 360-540 nm using laser ablation technique.

2. Experimental

The silicon rod (purity 99.999%, Goodfellow, U. K.) was clamped inside the laser ablation chamber. The ablation chamber was flushed with argon gas (purity 99.999%) two to three times after evacuation to remove the impurities. The third harmonic, 355 nm, of Pulsed Nd: YAG laser (120 mJ, Spectra Physics, USA) was focused on the target, rotating and translating with the help of stepper motor at a speed of 1 rpm, using a convex lens of focal length 50 cm. The produced plasma was allowed to cool adiabatically and the radiations from the cooled plasma was collected, using a cylindrical

lens of 25 cm, on the entrance slit of Spex TRIAX 320 M monochromator (Jobin Yvon, USA) fitted with TE cooled ICCD detector (Jobin Yvon, USA) system. The spectra of Si₂ molecule were recorded at delay time 220 ns with 5 accumulations in gated mode of ICCD and at pressure of 10^{-1} torr argon gas because most of the previously reported were appear at this delay time and pressure. The data acquisition in the computer was made using Spectra Max and Grams 32 software. The spectra of Si₂ molecule were recorded in the region of 360-540 nm using 1200 grs/mm grating blazed at 330 nm. Due to blazing, a process of cutting the grooves of a grating to a certain shape, the most of the light intensity is concentrate in the first order spectrum. However, to avoid the scattering and higher order spectrum, bandpass filter was used. The spectral resolution and spectral dispersion of the monochromator are 0.06 nm and 2.64 nm respectively for 1200 grs/mm grating. The schematic diagram of experimental arrangement is shown in Figure 1.

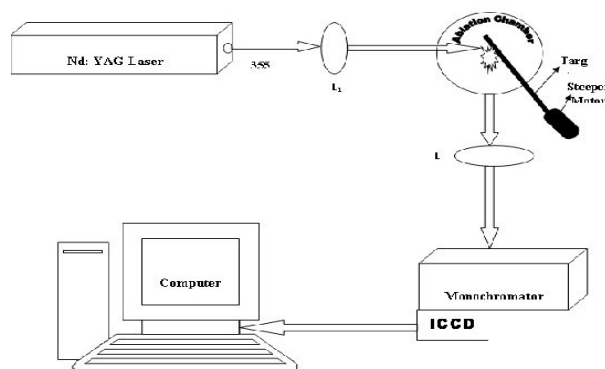


Figure 1. EXPERIMENTAL SETUP

Fig. 1 Experimental Setup

3. Analyses and Results

The laser-produced spectra of silicon dimer were recorded 360-540 nm in region. About 100 bands were observed and classified into three transitions. Out of three transitions, two transitions namely H'-X and I-X were new while the rest third was previously reported H-X transition. Out of total 100 bands, 55 bands were assigned into two new transitions while the rest 45 bands were assigned to H-X transition. The system wise analyses of the band systems were as given below.

3.1. New I – X System

The I-X system also lay in the region of H-X system. About 30 violet degraded and single headed bands were analyzed into $\Delta v = 0, \pm 1, -2, -3, -4$ and -5 sequences. The (0,0) band of this system was observed at 374.65 nm. The band lying at 372.38 nm reported by Dubois and Leclercq¹⁰ was assigned as (1,1) band. The bandhead data of I-X system are given in Table 1 and the spectrum is presented in Figure 2. The molecular constants of the system were as follows;

$$\begin{aligned} v_e &= 26580.04 \text{ cm}^{-1} & \omega_e'x_e' &= 3.85 \text{ cm}^{-1} & \omega_e'y_e' &= 0.07 \text{ cm}^{-1} \\ \omega_e' &= 720.0 \text{ cm}^{-1} & \omega_e''x_e'' &= 2.02 \text{ cm}^{-1} & \omega_e''y_e'' &= 0.15 \text{ cm}^{-1} \\ \omega_e'' &= 510.98 \text{ cm}^{-1} \end{aligned}$$

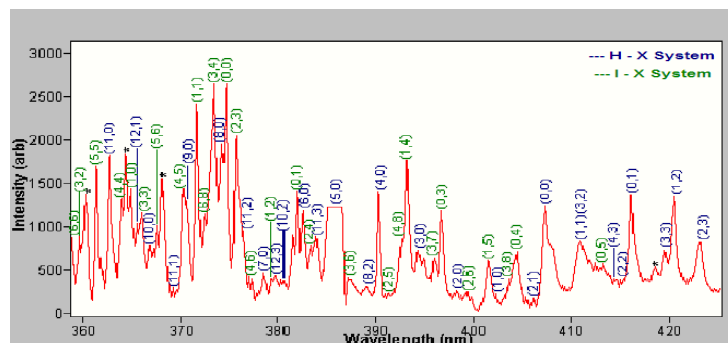


Fig.2 Laser Produced Spectrum of H-X and I-X System of Si₂ Molecule

Table 1. Bandhead Data of I - X System

v'	λ (nm, air)	v	v'	λ (nm, air)	v
3,2	359.71	27792.36	4,6	377.29	26497.36
1,0	364.97	27391.81	3,5	380.37	26282.80
6,6	359.37	27818.65	2,4	383.31	26081.21
5,5	361.45	27658.57	5,8	382.51	26135.76
4,4	363.89	27473.11	3,6	387.17	25821.20
3,3	366.05	27311.00	2,5	391.01	25567.60
1,1°	371.05	26942.97	1,4	393.15	25428.43
0,0	374.65	26684.08	0,3	396.71	25200.24
5,6	367.63	27193.62	4,8	392.75	25454.33
4,5	370.27	26999.73	3,7	396.04	25242.88
3,4	373.58	26760.50	2,6	399.20	25043.06
2,3	375.67	26611.62	1,5	401.48	24900.84
1,2	379.30	26356.94	0,4	404.57	24710.65
0,1	381.96	26173.40	3,8	403.70	24763.91
6,8	372.46	26840.97	0,5	413.17	24196.31

Band reported by Dubois and Leclercq

3.2. $H^3\Sigma_u^- - X^3\Sigma_g^-$ System

$H^3\Sigma_u^- - X^3\Sigma_g^-$ system has been identified in the region of 362-470 nm. The (0,0) band was observed at 407.30 nm for the first time. Total 43 bands were observed and analyzed into $\Delta v = 0, \pm 1, \pm 2, + 3, \pm 4, \pm 5, + 6, + 7, + 8, + 9, + 10$ and $+ 11$ sequences of the system. Out of total 9 bands reported by Douglas³, 8 bands had been fitted. The three bands reported by Verma and Warsop⁴, lying at 394.21 nm, 390.08 nm and 386.33 nm, were assigned as (3,0), (4,0) and (5,0) respectively in the proposed analysis. Out of 18 bands reported by Dubois and Leclercq⁹⁻¹⁰, 9 bands lying in this region were assigned as (3,8), (2,7), (1,6), (6,0), (7,0), (8,0), (11,1), (10,0) and (11,0) while one band lying at 360.24 nm had been assigned to I-X system. The rest 8 bands laying in the region 343-357 nm could not be detected due to poor response of ICCD in this region. The vibrational constants determined for both the electronic states were same as reported by Verma and Warsop⁴. The bandhead data of the system are given in Table 2 and the spectra are displayed in Figures 2 and 3.

Table 2. Bandhead Data of H - X System

v', v''	λ (nm, air)	v	v', v''	λ (nm, air)	v
12,1	365.33	27364.82	4,4	423.00	23634.02
11,0°	362.71	27562.50	3,3	419.58	23826.66
11,1°	369.20	27077.98	2,2	415.33	24070.47
10,0°	366.89	27248.46	1,1	411.15	24315.20
12,3	379.76	26325.02	0,0	407.31	24544.42
11,2	376.47	26555.07	2,3	423.21	23622.30
9,0	370.66	26971.32	1,2	420.52	23773.40
11,3	383.86	26043.84	0,1	416.14	24023.62
10,2	380.70	26260.02	6,8	451.46	22144.13
8,0°	374.67	26682.65	4,6 ⁺	443.15	22559.38
7,0°	378.55	26409.16	3,5 ⁺	437.93	22828.28
8,2	389.04	25697.07	2,4 ⁺	433.65	23053.60
6,0°	382.56	26132.34	1,3	430.48	23223.35
5,0 ^{*#}	386.11	25892.07	0,2	426.95	23415.36
4,0 [#]	390.33	25612.15	2,6 ⁺	453.00	22068.85
3,0 [#]	394.24	25358.13	1,5 ⁺	448.73	22278.85
2,0 ⁺	398.35	25096.50	0,4 ^x	443.83	22524.82
4,3	414.46	24121.00	3,8°	469.03	21314.60
3,2 ^x	410.95	24327.02	2,7°	463.92	21549.38
2,1 ⁺	406.10	24617.55	1,6°	458.34	21811.73
1,0	402.26	24852.56	0,5	454.31	22005.21
5,5 ⁺	428.31	23341.01			

* band overlapped by atomic line; ⁺ bands reported by Douglas

[#] bands reported by Verma and Warsop; ° Bands reported by Dubois and Leclercq

The modified molecular constants of the system were as given below;

$$\begin{aligned} v_e &= 24663.03 \text{ cm}^{-1} & \omega_e'x_e' &= 1.99 \text{ cm}^{-1} & \omega_e'y_e' &= 0.20 \text{ cm}^{-1} \\ \omega_e' &= 271.32 \text{ cm}^{-1} & \omega_e''x_e'' &= 2.02 \text{ cm}^{-1} & \omega_e''y_e'' &= 0.15 \text{ cm}^{-1} \\ \omega_e'' &= 510.98 \text{ cm}^{-1} \end{aligned}$$

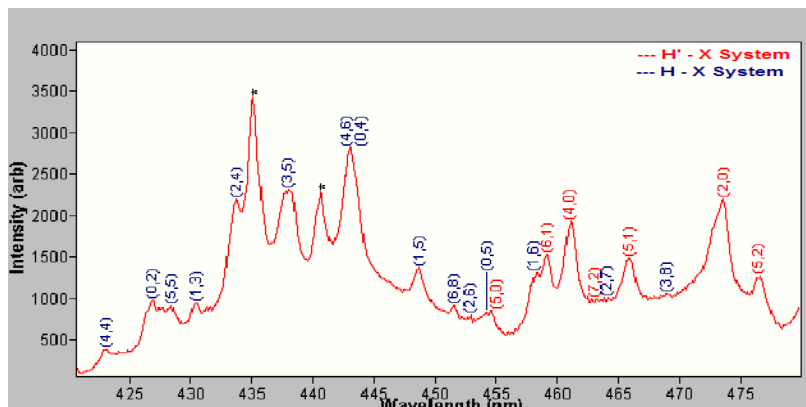


Fig.3 Laser Produced Spectrum of H-X and H'-X System of Si₂ Molecule

3.3. New H'-X System

H'-X system was identified in the region of 454-540 nm. The bands of this system were single headed and red degraded with (0,0) at 487.84 nm. The total 25 bands were observed and analyzed into $\Delta v = 0, \pm 1, \pm 2, \pm 3, + 4$ and $+ 5$. The bandhead data of the system are given in Table 3 and the spectra are presented in Figures 3 and 4. The molecular constants of this system were as given below;

$$\begin{aligned} v_e &= 20605.63 \text{ cm}^{-1} & \omega_e' &= 295.0 \text{ cm}^{-1} & \omega_e'x_e' &= 1.40 \text{ cm}^{-1} \\ \omega_e'y_e' &= 0.19 \text{ cm}^{-1} & \omega_e'' &= 510.98 \text{ cm}^{-1} & \omega_e''x_e'' &= 2.02 \text{ cm}^{-1} & \omega_e''y_e'' &= 0.15 \text{ cm}^{-1} \end{aligned}$$

Table 3. Bandhead Data of H' - X System

v', v''	λ (nm, air)	v	v', v''	λ (nm, air)	v
7,2	463.33	2157	1,1	493.15	20272.
6,1	459.17	21772.	0,0	487.84	20492.
5,0	454.66	2198	4,5	522.40	19137.
5,1	465.94	2145	1,2	506.10	19753.
4,0	461.08	2168	3,4	515.93	19377.
5,2	476.74	2096	0,1	500.90	19958.
5,3	490.26	2039	2,4	524.37	19065.
4,2	484.48	2063	1,3	518.82	19269.
2,0	473.66	2110	0,2	514.56	19428.
5,4	501.59	1993	2,5	538.01	18581.
4,3	496.39	2013	1,4	531.42	18812.
1,0	480.29	2081	0,3	527.37	18956.
3,3	503.33	1986			

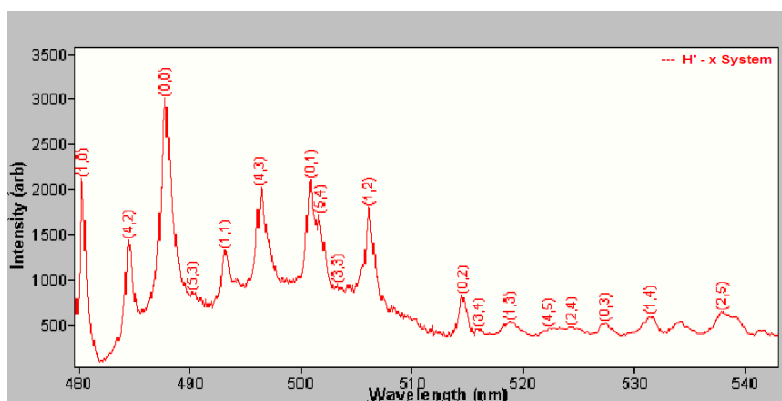


Fig.4 Laser Produced Spectrum of H-X and H'-X System of Si₂ Molecule

4. Discussion

From the above analysis, it is clear that all these three transitions had a common lower state i.e. $X^3\Sigma_g^-$. The vibrational constants determined for the $X^3\Sigma_g^-$ state were in close agreement to that reported by Verma and Warsop⁴. Also, the bands reported by Douglas³, Verma and Warsop⁴ and Dubois and Leclercq¹⁰ were observed and nicely fitted into $H^3\Sigma_u^- - X^3\Sigma_g^-$ system. On the basis of rotational studies by Douglas³, Verma and Warsop⁴, Dubois and Leclercq¹⁰, Kitsopoulos *et al.*¹³ and Fluara *et al.*¹⁵ and theoretical studies by Redondo *et al.*⁵ and Bruna *et al.*¹¹, had been shown that the ground state of Si₂ molecule was $^3\Sigma_g^-$ which arises from the configuration $\pi_u^2\sigma_g^2$ while the next low lying state was $^3\Pi_u$ which comes from the configuration $\pi_u^3\sigma_g$. Thus it is clear that the ground state $X^3\Sigma_g^-$ and next low lying state $D^3\Pi_u$ arise from electronic configurations $\pi_u^2\sigma_g^2$ and $\pi_u^3\sigma_g$ respectively while the low lying electronic states observed in the present analysis were arise from the electronic configurations $\pi_u^3\sigma_g, \pi_u^4$ and $\pi_u^2\sigma_g^2$.

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