

Infrared Laser Spectrum of the Si_2^- Anion in a Silane Plasma

Zhuan Liu and Paul B. Davies

*Department of Chemistry, University of Cambridge, Lensfield Road,
Cambridge CB2 1EW, United Kingdom*

(Received 11 September 1995)

The first rotationally resolved spectrum of the Si_2^- anion has been detected. The spectrum was recorded in a low pressure air cooled discharge in mixtures of silane and hydrogen producing amorphous silicon, using infrared laser velocity modulation absorption spectroscopy. Seventy lines between 740 and 820 cm^{-1} were assigned to the $A^2\Pi_{u1/2}(\nu = 1) \leftarrow X^2\Sigma_g^+(\nu = 0)$ subband of Si_2^- . A fit by standard Hamiltonians gives precise rotational and fine structure constants for the anion.

PACS numbers: 33.20.Ea, 33.15.Mt, 36.20.Kd, 36.40.Mr

The reactive silicon molecules generated in silane plasmas used to produce semiconductor material are of considerable structural and practical interest. Infrared laser and submillimeter-wave spectra of neutral and cation hydrides containing one or two silicon atoms, e.g., Si_2H_2 [1], SiH_5^+ [2], and SiH_7^+ [3], have been observed, thereby leading to a better understanding of their structure. These species have nonclassical [1] or cluster geometries [2,3], presenting a challenge for theory and an interesting contrast with their carbon analogs. While high resolution spectroscopy is leading to steady progress in determining the structure of silicon containing cations, no comparable studies of silicon anions have been reported. The available data on species like SiH_3^- are derived from low resolution techniques like photoelectron spectroscopy [4] supported by *ab initio* calculations [5].

Bare silicon clusters and their anions (Si_n , Si_n^- , $n = 2-10$) have attracted much attention because of their role in inhibiting the growth of device grade surfaces in silane plasmas and, more fundamentally, in understanding cluster structure [6] and distribution patterns (magic numbers) [7]. However, until recently there was a paucity of information even on the simplest silicon cluster anion, Si_2^- . Some limited structural data on Si_2^- are available from low resolution photoelectron [8,9] and threshold photodetachment (ZEKE) [9] spectroscopies. Two electronic states have been identified, $^2\Sigma_g^+$ and $^2\Pi_u$, lying very close to each other. The former arises from a $\sigma_g\pi_u^4$ electronic configuration and the latter from $\sigma_g^2\pi_u^3$, giving rise to an inverted $^2\Pi_u$ state. Initially the $^2\Pi_u$ state was believed to be the ground state, but a reassignment of the photodetachment spectra led to a reversal of their order [10]. The experimentally determined splitting (T_e) between the $^2\Sigma_g^+$ and $^2\Pi_u$ states is $25 \pm 10\text{ meV}$ ($200 \pm 80\text{ cm}^{-1}$) [10], in satisfactory agreement with high precision *ab initio* calculations (22 meV , 180 cm^{-1}) [11] which also concluded that the $^2\Sigma_g^+$ state was the ground state. The status of the high resolution spectroscopy of Si_2^- contrasts with that of C_2^- . There have been a number of studies of C_2^- since Herzberg and Lagerqvist [12] first detected its visible absorption and emission spectra, cul-

minating in the work of Oka and co-workers [13] on the hitherto undetected $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ system. In this Letter we describe the first high resolution spectrum of Si_2^- , arising from the analogous transition in this anion, observed by infrared laser spectroscopy.

The absorption spectrum of Si_2^- was recorded in a low pressure 45 kHz discharge in mixtures of silane and hydrogen using the diode laser spectrometer used earlier to detect SiH_3^+ [14]. The air cooled Pyrex discharge tube was 90 cm long and 9 mm internal diameter, and frequently needed cleaning or replacing due to copious deposition of amorphous silicon. The conditions required for optimum anion signals were similar to those for SiH_3^+ , namely, $\text{SiH}_4:\text{H}_2$ ratios of 1:10 at a total pressure of around 1 Torr and discharge currents up to 80 mA with a voltage of 4 kV. The anion lines were detected using the velocity modulation technique [15] and had a maximum signal to noise ratio of 16:1 with a 300 msec time constant. Seven lead salt diode lasers were used to provide $\sim 50\%$ spectral coverage in the appropriate region. Ion lines were calibrated to an accuracy of 0.003 cm^{-1} using C_2H_2 and NH_3 calibration spectra.

Figure 1 shows a representative spectrum of Si_2^- . The spectrum also contains cation lines which appear with opposite phase. The absolute phase was determined by recording known cation spectra, e.g., of H_3O^+ . The initial group of anion lines, found near 810 cm^{-1} , was thought to arise from SiH_3^- , which has a fundamental band (ν_2) predicted to lie close to this region ($\sim 870\text{ cm}^{-1}$) [5]. However, as more lines were recorded between 740 and 850 cm^{-1} this assignment was rejected for several reasons. First, the spectrum lacked the characteristic symmetric top structure expected for SiH_3^- . Second, most of the lines appeared well below the predicted band origin, i.e., outside any reasonable uncertainty in the *ab initio* calculation. Third, the spectrum terminated sharply at $\sim 820\text{ cm}^{-1}$. Finally, the anion linewidths were slightly narrower than those of neighboring SiH_3^+ lines. Although this characteristic is not in itself a quantitative guide to the nature of the carrier, it did suggest a species with more than one heavy atom. When the data from the

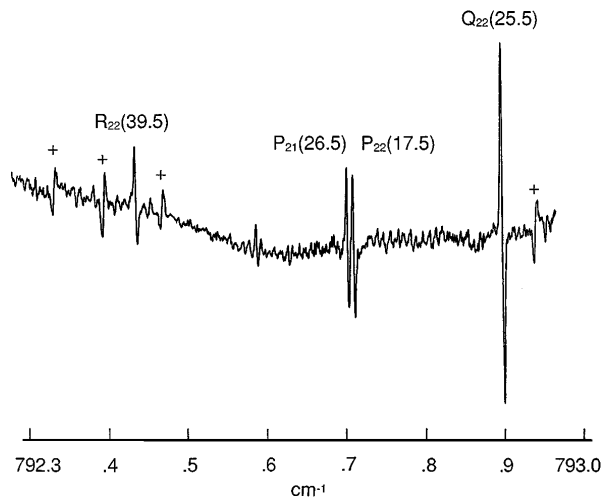


FIG. 1. Assigned lines forming part of the $A^2\Pi_{u1/2}(v=1) \leftarrow X^2\Sigma_g^+(v=0)$ subband of Si_2^- recorded in a silane plasma using infrared laser velocity modulation spectroscopy. Lines indicated by (+) are cation lines appearing with opposite phase to the anion lines.

reinterpreted ZEKE spectrum [10] of Si_2^- were evaluated it became clear that the new spectrum was most likely due to the $A^2\Pi_{u1/2}(v=1) \leftarrow X^2\Sigma_g^+(v=0)$ transition of Si_2^- . Although subject to an uncertainty of $\pm 80 \text{ cm}^{-1}$, the origin of this band derived from low resolution results is 794 cm^{-1} .

The rotational transitions of the three main branches of a $^2\Pi_{u1/2} \leftarrow ^2\Sigma_g^+$ subband, P_{22} , Q_{22} , and R_{22} , should follow a polynomial in J : $\tilde{\nu} = a + bJ + cJ^2$ [16]. The assignment was initiated by identifying ten transitions, spread over many laser modes, which fitted this polynomial with coefficients $b = -0.287 \text{ cm}^{-1}$ and $c = -0.0185 \text{ cm}^{-1}$. This value of b is very close to that estimated from $B' - 2B''$ using the low resolution internuclear distances for the $^2\Sigma$ and $^2\Pi$ states [8,9], and identified this branch as Q_{22} . Combining b and c ($\approx B' - B''$) enabled B' and B'' to be separated and members of the P_{22} and R_{22} branches to be assigned. Transitions in the $Q_{21}(J)$ and $P_{21}(J)$ satellite branches could be identified because they are close to corresponding main branch components, $R_{22}(J-1)$ and $Q_{22}(J-1)$, respectively, from which they are separated by γJ , where γ is the spin rotation constant in the $^2\Sigma_g^+$ state. Lines in the R_{21} satellite branch were assigned once a more complete fit had been made. The assignment is unambiguous evidence for the ordering of the vibronic states involved in the spectrum; an alternative rotational assignment placing the $^2\Sigma_g^+$ vibronic state above the $^2\Pi_u$ state is impossible. This result consolidates the earlier evidence for the $^2\Sigma_g^+$ state as the ground state. As expected from nuclear spin statistical factors (^{28}Si , $I = 0$) negative parity rotational levels are missing in the lower state and positive parity levels are missing in the upper state, leading to the absence of Λ doublet splittings and instead a staggering

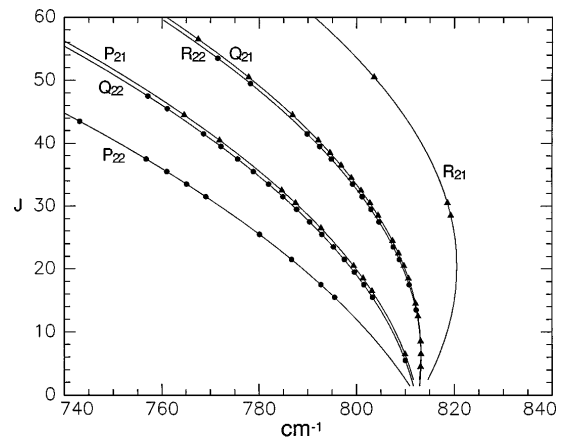


FIG. 2. Fortrat diagrams for the six branches of the $A^2\Pi_{u1/2}(v=1) \leftarrow X^2\Sigma_g^+(v=0)$ transition of Si_2^- . The curves were constructed from the fitted parameters given in Table II. The experimentally measured rotational components are indicated by (●) for the main branches and (▲) for the satellite branches.

of rotational levels. Figure 2 shows the Fortrat diagram of the six branches. The abrupt high wave-number termination of the spectrum just above a quite dense region of Si_2^- lines is explained by the red shading of the branches. A simulation of the spectrum using a rotational temperature of 570 K, known to be qualitatively correct for silicon hydride cations in the same discharge [14], showed that the bandhead in the R_{21} satellite branch was too weak to detect.

The Franck-Condon factors were calculated for Morse potential functions using *ab initio* values of ω_e , $\omega_e x_e$, and r_e from the results of Nimlos, Harding, and Ellison [8]. They are similar to those of C_2^- between the same vibrational levels of the A and X states. However, the most intense band $(v', v'') = (0, 0)$, which in C_2^- has an origin at 3929 cm^{-1} [13], lies in the far infrared region ($\sim 200 \text{ cm}^{-1}$) in Si_2^- , outside the range of diode lasers. Among other low lying vibrational levels the observed band (1, 0) is among the strongest. In other regions accessible with diode lasers the (2, 0) band at 1220 cm^{-1} ($^2\Pi_{3/2} \leftarrow ^2\Sigma$) and 1340 cm^{-1} ($^2\Pi_{1/2} \leftarrow ^2\Sigma$) is also strong with a Franck-Condon factor about a quarter of the (1, 0) value. A search revealed lines with the same chemical characteristics as Si_2^- in both regions. However, insufficient laser coverage prevented the recording of sufficiently large sections of the spectrum to make an assignment. Since the $^2\Pi$ state is only $\sim 200 \text{ cm}^{-1}$ above the ground state, it is reasonable to assume a considerable population of at least the $v = 0$ level in the discharge. The Franck-Condon factors for several vibronic transitions originating from the $^2\Pi$ state are large enough to warrant future searches.

The data for the subband were fitted by the Hamiltonians used by Miller, Suzuki, and Hirota [17] for $^2\Sigma$ and $^2\Pi$ states in their analysis of the analogous A-X system of

N_2^+ . Representative assigned lines and their fitted values are given in Table I. A least squares fit of over seventy lines to eight parameters yielded the results in Table II with a standard deviation of 0.0036 cm^{-1} . Without data from the other subband ${}^2\Pi_{u3/2}(v=1) \leftarrow {}^2\Sigma_g^+(v=0)$, the spin orbit constant A could not be determined and only the combination of parameters, $T_{10} - A/2$, was well determined. In the fit the constant A was fixed at its low resolution value of -122 cm^{-1} . If the $v=0-1$ spacing of $533(\pm 5) \text{ cm}^{-1}$ is adopted for the ${}^2\Pi$ state [10], then the present results give $T_{00} = 218 \text{ cm}^{-1}$. This is in satisfactory agreement with experimental and theoretical values of T_e . The values of the internuclear distances in the lower and upper states derived from the accurate rotational constants in Table II are $r_0 = 2.113\,616(11) \text{ \AA}$ and $r_1 = 2.192\,150(14) \text{ \AA}$. In the absence of vibration-rotation constants (α_e) from the experiment we have calculated them from *ab initio* data and combining these with the experimental B values yields $r_e(X^2\Sigma) = 2.1104 \text{ \AA}$ and $r_e(A^2\Pi) = 2.1798 \text{ \AA}$. These are very close to the photoelectron results both for the ${}^2\Sigma$ state (2.127 [8] and 2.116 \AA [9]) and for the ${}^2\Pi$ state (2.187 [8] and 2.207 \AA [9]). The most recent *ab initio* values 2.092 [11] and 2.160 \AA [8] (${}^2\Sigma$ state) and 2.159 [11] and 2.197 \AA [8] (${}^2\Pi$ state) bracket the present experimental results.

The absence of any anion signals which could be attributed to SiH_3^- merits comment. Shen and co-workers [5] predicted that this species should have quite an intense fundamental close to the search region. It suggests

TABLE I. Representative spectral lines (cm^{-1}) in the $A^2\Pi_u(v=1) \leftarrow X^2\Sigma_g^+(v=0)$ band of Si_2^- .

Branch	J''	$\tilde{\nu}_{\text{obs}}$	$\tilde{\nu}_{\text{obs}} - \tilde{\nu}_{\text{cal}} (\times 10^3)$
Q_{22}	31.5	784.897	-2
	29.5	787.710	-3
	27.5	790.382	1
	25.5	792.903	0
	23.5	795.282	5
	21.5	797.507	2
P_{21}	30.5	787.489	-3
	26.5	792.717	1
	20.5	799.433	-3
Q_{21}	30.5	802.775	-1
	28.5	804.463	3
	24.5	807.385	0
	22.5	808.621	-5
	20.5	809.715	-5
R_{22}	29.5	802.997	0
	27.5	804.672	5
	23.5	807.561	-2
	21.5	808.792	3
	P_{22}	31.5	769.082
P_{21}	25.5	780.092	3
	21.5	786.694	-3
	R_{21}	30.5	818.589
	28.5	819.282	4

that the plasma chemistry is similar to that observed by Perrin *et al.* [18] in their study of a low pressure, low current multipole discharge in silane. At the lowest pressures they used (0.2 mTorr) they found that the ion signals of Si_2^- and SiH_3^- were closely similar, but at higher pressures (up to 10 mTorr) the Si_2^- signal was tenfold larger than SiH_3^- . They proposed that Si_2^- was mainly produced by hydrogen elimination when disilicon hydride anions like Si_2H_2^- react with silane. In fact, other than at the lowest silane pressures, mass spectrometric results generally show that disilicon anions are the most abundant species. In rf deposition plasmas at even higher pressures (~ 70 mTorr) [19] the dominant silicon anion is Si_2H_5^- . Although it is important to remember that the plasma in the present experiment uses much higher relative proportions of H_2 , for reasons of stability, it will be worthwhile investigating the silane plasma over a wider range of compositions and pressures as a source of other new spectra. These would obviously include the spectra of SiH_3^- and Si_2H_5^- . Silicon hydride anions are also the primary source of particulate contamination in rf silane deposition plasmas [19,20], an important factor limiting the quality of amorphous silicon they produce. The infrared absorption spectrum of Si_2^- could provide a convenient non-invasive method for investigating anion behavior in such plasmas. Finally, bearing in mind the success of high resolution ir laser spectroscopy in detecting bare carbon clusters [21] the extension of the present work to larger silicon clusters should be considered. Raghavachari and Rohlfing [11] have calculated structures and vibrational frequencies for Si_3^- (and higher clusters). Si_3^- has C_{2v} symmetry and two low lying electronic states with at least one vibrational mode accessible to diode laser spectroscopy.

We thank the Cambridge Overseas Trust and Unilever Research for financial support for one of us (Z.L.). We are very grateful to Dr. P.M. Martineau and Dr. D.M. Smith for helpful information and preliminary studies on the anions in silane discharges, and Dr. D. Husain for use of a Franck-Condon factor calculation program. Dr. N.A. Martin kindly loaned us some of the diodes used in this project.

TABLE II. Spectroscopic constants (cm^{-1}) of the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states of Si_2^- (1σ uncertainties in the last digits in parentheses).

	${}^2\Pi_u(v=1)$		${}^2\Sigma_g^+(v=0)$
T_{10}	751.2795(11)		
A	-122^a		
B	0.250 776(23)	B	0.269 758(23)
D	$2.39(7) \times 10^{-7}$	D	$2.60(7) \times 10^{-7}$
p	$-4.88(87) \times 10^{-4}$	γ	$7.247(33) \times 10^{-3}$
q	$-1.36(99) \times 10^{-5}$		

^aFixed at the value from photoelectron spectroscopy [10].

- [1] M. Bogey, H. Bolvin, C. Demuynck, and J.L. Destombes, *Phys. Rev. Lett.* **66**, 413 (1991); M. Cordonnier, M. Bogey, C. Demuynck, and J.L. Destombes, *J. Chem. Phys.* **97**, 7984 (1992); M. Bogey, H. Bolvin, M. Cordonnier, C. Demuynck, J.L. Destombes, and A.G. Csaszar, *J. Chem. Phys.* **100**, 8614 (1994).
- [2] D. W. Boo and Y. T. Lee, *J. Chem. Phys.* **103**, 514 (1995).
- [3] Y. Cao, J-H. Choi, B-M. Haas, M.S. Johnson, and M. Okumura, *J. Phys. Chem.* **97**, 5215 (1993).
- [4] M.R. Nimlos and G.B. Ellison, *J. Am. Chem. Soc.* **108**, 6522 (1986).
- [5] M. Shen, Y. Xie, and H.F. Schaefer, *J. Chem. Phys.* **93**, 8098 (1990); M. Shen, Y. Xie, Y. Yamaguchi, and H.F. Schaefer, *J. Chem. Phys.* **94**, 8112 (1991).
- [6] N. Binggeli and J.R. Chelikowsky, *Phys. Rev. Lett.* **75**, 493 (1995).
- [7] *Physics and Chemistry of Small Clusters*, edited by P. Jena, B.K. Rao, and S.N. Khanna, NATO ASI Ser. B, Vol. 158 (Plenum, New York, 1987).
- [8] M.R. Nimlos, L.B. Harding, and G.B. Ellison, *J. Chem. Phys.* **87**, 5116 (1987).
- [9] T.N. Kitsopoulos, C.J. Chick, Y. Zhao, and D.M. Neumark, *J. Chem. Phys.* **95**, 1441 (1991).
- [10] C.C. Arnold, T.N. Kitsopoulos, and D.M. Neumark, *J. Chem. Phys.* **99**, 766 (1993).
- [11] K. Raghavachari and C.M. Rohlring, *J. Chem. Phys.* **94**, 3670 (1991).
- [12] G. Herzberg and A. Lagerqvist, *Can. J. Phys.* **46**, 2363 (1968).
- [13] B. D. Rehfuss, D.J. Liu, B. M. Dinelli, M.F. Jagod, W.C. Ho, M.W. Crofton, and T. Oka, *J. Chem. Phys.* **89**, 129 (1988).
- [14] D.M. Smith, P.M. Martineau, and P.B. Davies, *J. Chem. Phys.* **96**, 1741 (1992); P.B. Davies and D.M. Smith, *J. Chem. Phys.* **100**, 6166 (1994).
- [15] C.S. Gudeman, M.H. Begemann, J. Pfaff, and R.J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).
- [16] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950), 2nd ed., p. 261.
- [17] T.A. Miller, T. Suzuki, and E. Hirota, *J. Chem. Phys.* **80**, 4671 (1984).
- [18] J. Perrin, A. Lloret, G. De Rosny, and J.P.M. Schmitt, *Int. J. Mass Spec. Ion Proc.* **57**, 249 (1984).
- [19] A.A. Howling, J.-L. Dorier, and Ch. Hollenstein, *Appl. Phys. Lett.* **62**, 1341 (1993).
- [20] A.A. Howling, L. Sansonnens, J.-L. Dorier, and Ch. Hollenstein, *J. Appl. Phys.* **75**, 1340 (1994).
- [21] J.R. Heath and R.J. Saykally, *J. Chem. Phys.* **94**, 1724 (1991).