Electronic Absorption Spectra of Si_n and Si_n^- (n = 2-4) in Neon Matrices

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Electronic absorption spectra of silicon molecules Si_n and Si_n^- (n=2-4) in 5 K neon matrices have been observed. The approach is based on mass-selection and codeposition with neon. The neutral species become apparent after photodetachment. The band systems detected are assigned using available calculations and photoelectron spectra. In the case of Si_3 (C_{2v}), electronic transitions from the X 1A_1 ground state to the excited electronic states 1B_1 , 1A_1 , 1B_1 , and 1B_2 have been identified. Their O_0^0 bands are at 778.9, 579.7, 522.3, and 388.3 nm, respectively. Two band systems, with origin bands at 925.3 and 466.6 nm, are assigned to the $^1B_{3u} \leftarrow X$ 1A_g and $^1B_{1u} \leftarrow X$ 1A_g transitions of Si_4 (D_{2h}). Two known electronic transitions are obtained for Si_2 , but a reported band system with origin at 288.3 nm cannot be due to this molecule. The following electronic transitions were detected for the anions: Si_2 , $^2T_u \leftarrow X$ $^2S_g^+$; Si_3 $^-$ (C_{2v}), $^2A_1 \leftarrow X$ 2A_1 ; Si_4 $^-$ (D_{2h}), $^2B_{1u} \leftarrow X$ $^2B_{2g}$, with origin bands at 432.7, 1036.7, and 872.6 nm. Vibrational frequencies of several totally symmetric modes could be inferred for the studied species in the electronic excited states.

Introduction

Silicon clusters have drawn the attention of many investigators. Photofragmentation of silicon cluster ions, 1,2 photoionization, 3,4 and chemical reactions 5,6 have been studied by mass spectrometry. Quantum-mechanical calculations of the structures and stability of such systems in the ground state have been carried out. $^{7-11}$

Photoelectron spectra of $\mathrm{Si_2}^-$, $\mathrm{Si_3}^-$, and $\mathrm{Si_4}^-$ have been reported. In the case of $\mathrm{Si_2}$, this localized the five lowest lying excited electronic states in the energy region up to 1.16 eV above the ground state. Analysis of the $\mathrm{Si_3}^-$ and $\mathrm{Si_4}^-$ spectra yielded, in addition to the positions of the electronic states, the frequencies of some of the vibrational modes.

Electronic absorption or emission spectroscopy is an alternative source of information. Absorption spectra of mass-selected carbon chains C_{2n}^- (n=2-10) trapped in neon matrices have recently been identified.^{18,19} However, such observations on silicon species are, with the exception of Si₂, scarce.²⁰⁻²³ In this work electronic transitions of Si_n and Si_n⁻ (n=2-4) have been detected using the technique combining mass-selection and matrix isolation spectroscopy.

Experimental Section

The approach of mass-selection combined with matrix absorption spectroscopy was used. Si_n species were produced by bombarding a silicon rod with Cs⁺. Si_n species were produced by bombarding a silicon rod with Cs⁺. Si_n species were produced anion formation decreased rapidly with the size of the clusters, restricting the study of the species for $n \le 4$. The anions were extracted from the ion source, deflected by 90°, and led through a quadrupole mass-selector. The ions of interest were deposited with about 50 eV kinetic energy together with excess of neon on a rhodium-coated sapphire plate held at 5 K. Typical ion currents measured at the matrix substrate prior to deposition were 900 nA (Si₂⁻), 200 nA (Si₃⁻), and 18 nA (Si₄⁻). Photobleaching after deposition was used to confirm that the observed spectra are of the anions. To study the neutral silicon

molecules, the surface of the matrix was irradiated with the UV light from a 80 W medium-pressure mercury lamp during deposition. This caused electron photodetachment, yielding a matrix containing mass-selected neutral species.

The absorption spectra of the trapped species were recorded in the 230–1100 nm region using a single beam spectrometer with a resolution of 0.1 nm. The matrix was probed by monochromatic light in a waveguide manner through a path length of 20 mm.²⁷ The signal was detected with a photomultiplier (230–600 nm) or a Si diode detector (600–1100 nm).

Results and Discussion

A. Si₂. Three electronic transitions of Si₂ which are in the covered spectral range are known. The H $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ band system is in the region 340–415 nm, though the origin is not established. The K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition has its origin at \sim 325 nm. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition, a strong absorption system with origin at 288.3 nm, which was tentatively assigned to the D $^3\Pi_u \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ transition of Si₂. Vacuum—UV photolysis of silane trapped in an argon matrix yielded, besides the K $^3\Sigma_u^- \leftarrow X$ $^3\Sigma$

MRD-CI *ab initio* calculations place the D $^3\Pi_u$ state close to the ground state. 31,32 A SCF-MRCI calculation on Si₂ predicts a $^3\Pi_u$ state to be 42 200 cm $^{-1}$ above the ground state. 33 This is 7000 cm $^{-1}$ higher in energy than the observed electronic transition, but exceeds, according to the authors, the uncertainty.

The present observations on mass-selected Si_2 species show that the spectrum observed at 260-290 nm 21 cannot correspond to an electronic transition of Si_2 . Whereas the two H $^3\Sigma_u^- \leftarrow$ X $^3\Sigma_g^-$ and K $^3\Sigma_u^- \leftarrow$ X $^3\Sigma_g^-$ transitions of Si_2 are very intense in our spectra, absorption bands in the 260-290 nm region are not seen.

B. Si₂⁻. Photoelectron and photodetachment studies have identified the two lowest electronic states of Si₂⁻. ^{13,14} The ground state of Si₂⁻ is $^2\Sigma_g^+$, with a state of $^2\Pi_u$ symmetry lying 0.025 eV above.

Codeposition of mass-selected $\mathrm{Si_2}^-$ with neon is associated with the appearance not only of known absorption bands of $\mathrm{Si_2}$ but also of a band system with origin at 432.7 nm (Figure 1). UV irradiation of the matrix results in disappearance of this

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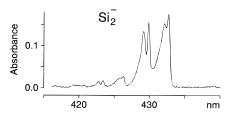


Figure 1. Electronic absorption spectrum of the ${}^2\Pi_u \leftarrow X$ ${}^2\Sigma_g^+$ transition of Si_2^- in a neon matrix. The spectrum was recorded after mass-selection and deposition of Si_2^- together with excess of neon on a 5 K substrate.

TABLE 1: Maxima of the Observed Bands in the ${}^2\Pi_u \leftarrow X \, {}^2\Sigma_g^+$ Electronic Transition of Si_2^- in a 5 K Neon Matrix g

$\lambda (\text{nm})^b$	$\nu (\mathrm{cm}^{-1})^c$	$\Delta \nu \ (\mathrm{cm^{-1}})$	assignment
432.7	23 111	0	$^{2}\Pi_{u} \leftarrow X^{2}\Sigma_{\sigma}^{+} 0 - 0 (\Omega = ^{3}/_{2})$
432.1	23 143	32	site
429.9	23 261	151	$0-0 \ (\Omega = \frac{1}{2})$
429.2	23 299	188	site
426.3	23 458	347	$1-0 (\Omega = \frac{3}{2})$
425.7	23 491	380	site
423.5	23 613	502	$1-0 \ (\Omega = \frac{1}{2})$
422.8	23 652	541	site

^a Transitions to the two spin-orbit components of the ${}^2\Pi_{\rm u}$ state are designated by $\Omega={}^3/_2$ and ${}^1/_2$. ${}^b\pm0.2$ nm. c The uncertainty can be derived from the first column.

absorption and in an increase in intensity of the bands due to Si_2 . Thus the spectrum in Figure 1 is attributed to an electronic transition of Si_2^- .

The observed absorption bands of $\mathrm{Si_2}^-$ are listed in Table 1. The origin of the electronic transition is 0.67 eV higher than the gas phase electron affinity of $\mathrm{Si_2}$ (2.20 eV). ¹⁴ As has been observed for anions of carbon chains isolated in neon matrices, ^{18,19} the stabilization by the surrounding neon atoms leads to an electron detachment energy which is ~ 1 eV larger than the gas phase electron affinity.

The allowed electronic transitions from the X $^2\Sigma_g^+$ ground state of $\mathrm{Si_2}^-$ are to states of $^2\Sigma_u^+$ or $^2\Pi_u$ symmetry. The 151 \pm 16 cm $^{-1}$ spacing between the first two bands (432.7 and 429.9 nm) in Figure 1 is attributed to spin—orbit splitting in the $^2\Pi_u$ electronic excited state. This value is comparable with the 122 \pm 10 cm $^{-1}$ separation observed for another $^2\Pi_u$ state (0.025 eV above the ground state) from the ZEKE spectrum. 14

Each band shows further doublet structure with an average spacing of ${\sim}35~\text{cm}^{-1}.$ This is site structure and comes from different orientations of the ions trapped in the solid neon. Such site effects can also be observed in the H $^3\Sigma_u^-\leftarrow X$ $^3\Sigma_g^-$ transition of Si $_2$. The quartet pattern is repeated for the less intense band at higher energy. The ${\sim}350~\text{cm}^{-1}$ separation corresponds to the vibrational frequency of Si $_2^-$ in the $^2\Pi_u$ excited state.

C. Si₃. Calculations on Si₃ predict two almost isoenergetic ground states. $^{34-37}$ In the $^{1}A_{1}$ state, Si₃ (C_{2v}) has a triangular geometry with an apex angle of 80° and a Si–Si bond length of 2.16 Å. The second state, $^{3}A'_{2}$ (D_{3h}), corresponds to an equilateral triangle with a bond length of 2.26 Å. Infrared spectra of silicon clusters produced by laser vaporization and trapped in rare gas matrices lead to the conclusion that the $^{1}A_{1}$ state (C_{2v} symmetry) is the ground state of Si₃. 38

Deposition of mass-selected $\mathrm{Si_3}^-$ anions exposed to UV light during the neon matrix formation is accompanied by the appearance of several absorption systems. Two intense systems are observed, 330–390 and 530–580 nm, as well as two weak systems in the 430–530 and 700–780 nm region (Figures 2 and 3).

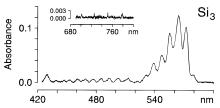


Figure 2. ${}^{1}B_{1} \leftarrow X {}^{1}A_{1}$ (430–530 nm), ${}^{1}A_{1} \leftarrow X {}^{1}A_{1}$ (530–580 nm), and ${}^{1}B_{1} \leftarrow X {}^{1}A_{1}$ (700–780 nm) electronic transitions of Si₃ in a 5 K neon matrix. The absorption spectra were measured after a mass-selected beam of Si₃⁻ was codeposited with excess of neon while irradiating with a medium-pressure mercury lamp.

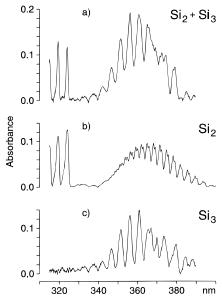


Figure 3. Trace a shows the absorption spectrum measured after codeposition of mass-selected Si_3^- and excess of neon under simultaneous irradiation with UV light. In trace b the H $^3\Sigma_u^- \leftarrow X$ $^3\Sigma_g^-$ electronic transition of Si_2 after deposition and UV irradiation of mass-selected Si_2^- in a 5 K neon matrix is shown. Subtraction of trace b from trace a after scaling results in the spectrum shown in trace c. This absorption band system is assigned to the $^1B_2 \leftarrow X$ 1A_1 electronic transition of Si_3 .

1. 700–780 nm System. In a photoelectron spectrum of $\mathrm{Si_3}^-$ a system with its origin lying 1.67 eV above the ground state of $\mathrm{Si_3}$ was observed. This was assigned to the $^1\mathrm{B_1}$ excited state. The matrix absorption spectrum of $\mathrm{Si_3}$ (700–780 nm; Figure 2) shows a system consisting of four weak bands (Table 2), energetically close to the photoelectron data. Supported by an *ab initio* calculation (second-order polarization propagator approximation 9) which predicts a $^1\mathrm{B_1}$ state 1.69 eV above the ground state, we assign the system to the $^1\mathrm{B_1} \leftarrow \mathrm{X}$ $^1\mathrm{A_1}$ transition of $\mathrm{Si_3}$ with origin band at 778.9 nm. The vibrational spacing of \sim 470 cm $^{-1}$ is close to the frequency inferred from the photoelectron spectrum (480 \pm 40 cm $^{-1}$). 15

2. 530–580 nm System. This band system has its origin at 579.7 nm, and the excitation of a vibrational mode with a frequency in the 235–270 cm⁻¹ range in the upper electronic state is discernible (Figure 2, Table 2).

Several weak absorption bands have previously been observed in the region 520-570 nm for silicon vapor trapped in a neon matrix. The wavenumbers of those bands are close to the values in Table 2. The absorption in this region was tentatively assigned to Si_4 . In the light of the mass-selection this attribution has to be corrected to a transition of Si_3 .

The excited electronic state of this transition has not been observed in the photoelectron spectrum of Si₃⁻ because it lies outside the energy accessible with the laser used.¹⁵ However,

TABLE 2: Observed Bands (Maxima) of the Four Electronic Transitions of Si_3 and Proposed Assignment ($C_{2\nu}$ Symmetry) in a 5 K Neon Matrix

$(C_{2v}$ Symme	ury) in a 5 K r	veon Matrix	
$\lambda (\mathrm{nm})^a$	$\nu (\mathrm{cm}^{-1})^b$	$\Delta \nu \ (\mathrm{cm}^{-1})$	assignment
778.9	12 839		${}^{1}B_{1} \leftarrow X {}^{1}A_{1} {}^{00}{}^{0}$
751.3	13 310	472	
725.1	13 791	481	1_0^1 1_0^2 1_0^3
701.4	14 257	466	1_0^3
579.7	17 250		${}^{1}A_{1} \leftarrow X {}^{1}A_{1} {}^{0}0$
571.9	17 486	235	2_0^1
564.1	17 727	242	2_0^2
554.8	18 025	297	2_0^3
546.7	18 292	267	2_0^4
538.6	18 567	275	2_0^5
531.1	18 829	262	2_{0}^{1} 2_{0}^{2} 2_{0}^{3} 2_{0}^{4} 2_{0}^{5} 2_{0}^{6}
522.3	19 146		${}^{1}B_{1} \leftarrow X {}^{1}A_{1} {}^{00}{}^{0}$
512.7	19 505	358	1_0^1
502.2	19 912	408	1_{0}^{1} 1_{0}^{2} 1_{0}^{3} 1_{0}^{4} 1_{0}^{5} 1_{0}^{6} 1_{0}^{7}
493.5	20 263	351	1_0^3
485.0	20 619	355	1_0^{4}
476.7	20 978	359	1_0^5
468.8	21 331	354	1_0^{6}
461.1	21 687	356	1_0^{7}
452.5	22 099	412	
446.9	22 376	277	
438.6 429.4	22 800 23 288	423 488	
		400	
388.3	25 753	249	${}^{1}B_{2} \leftarrow X {}^{1}A_{1} {}^{00}{}^{0}$
384.6 379.8	26 001 26 330	248 329	
373.6	26 767	437	
370.1	27 020	253	
367.1	27 241	221	
365.5	27 360	119	
361.0	27 701	341	
356.3	28 066	365	
351.7	28 433	367	
346.9	28 827	393	
342.2 337.6	29 223 29 621	396 398	
337.0	27 021	370	

 a ± 0.2 nm. b The uncertainty can be derived from the first column. c The position of the origin is tentative.

the energies of excited electronic states of Si_3 have been calculated.³⁹ This predicts two allowed electronic transitions which are in the range of the observed band system. One is a $^1A_1 \leftarrow X$ 1A_1 transition at 626 nm and the other $^1B_1 \leftarrow X$ 1A_1 at 574 nm (with oscillator strength of 0.002 and 0.008, respectively). A QCISD(T)/[7s6p3d1f] *ab initio* treatment predicts the 1A_1 excited state to be at \sim 534 nm.⁴⁰ On the basis of these calculations and the fact that there is another transition observed between 430 and 530 nm (see next section), it is assumed that the absorption in the 530–580 nm region is due to the $^1A_1 \leftarrow X$ 1A_1 electronic transition of Si_3 .

3. 430–530 nm System. A weak absorption band system between 430 and 530 nm is apparent (Figure 2). This cannot be part of the ${}^{1}A_{1} \leftarrow X {}^{1}A_{1}$ transition because the vibrational progression has a spacing of >350 cm⁻¹ as compared to the <270 cm⁻¹ value in the ${}^{1}A_{1}$ excited state. As it is not certain which band is the origin of this transition, it is given as tentative in Table 2.

Theory predicts that there is a ${}^{1}B_{1}$ electronic state close to the ${}^{1}A_{1}$ excited state, 2.16 eV (574 nm) above the ground state. 39 However, the calculated oscillator strength for ${}^{1}B_{1} \leftarrow X {}^{1}A_{1}$ (0.008) is greater than for the ${}^{1}A_{1} \leftarrow X {}^{1}A_{1}$ (0.002) transition. 39 Because calculated state energies are more reliable than the

oscillator strengths, the 430-530 nm weak band system is assigned to the ${}^{1}B_{1} \leftarrow X {}^{1}A_{1}$ electronic transition of Si₃.

4. 330-390 nm System. The absorption spectrum of Si₃ in the ultraviolet (330-390 nm) shows a complex band pattern (Figure 3a). This is partly due to overlap with weak absorption bands belonging to the H $^3\Sigma_{\rm u}^- \leftarrow {\rm X} \ ^3\Sigma_{\rm g}^-$ electronic transition of Si₂ (Figure 3b). The Si₂ molecule is present in the neon matrix as a result of fragmentation of Si3- during deposition (~50 eV kinetic energy) and/or by photodissociation of Si₃ on UV irradiation. The spectrum of Si₃ shown in Figure 3c is obtained by subtracting the spectrum of Si₂ (Figure 3b) from that of Figure 3a. The band positions are given in Table 2. On the higher energy side (λ < 366 nm) the band structure can be interpreted in terms of a vibrational frequency of ca. 350 cm⁻¹. Near the onset of the spectrum ($\lambda > 366$ nm) the vibrational structure is complex. Deconvolution does not lead to a clear pattern, though a second frequency in the 440–480 cm⁻¹ range is suggested.

According to the calculations for Si_3 the next allowed electronic transition (i.e., with large oscillator strength) is to a 1B_2 state, at an excitation energy of 3.38 eV (f = 0.043). The first absorption band in the low-energy part of the spectrum is at 388.3 nm (3.19 eV). The system consists of many broad bands of medium intensity leading to a large integrated intensity, supporting the assignment to the $^1B_2 \leftarrow X ^1A_1$ transition.

5. Si₃ **Emission Spectrum.** An emission spectrum of silicon vapor excited in a laser initiated plasma has been published.²³ Two emission band systems are observed, one between 420 and 450 nm and the other 490–530 nm. On the basis of erroneous interpretation of matrix data²⁰ (see section C.2), these bands were assigned to electronic transitions of Si₃. In the emission spectrum (420–450 nm) it was possible to discern a progression associated with a vibrational mode with frequency of 310 cm⁻¹ in the excited electronic state and a mode with frequency of 370 cm⁻¹ in the lower one. In the 490–530 nm region the emission spectrum comprises a 310 cm⁻¹ progression in the upper state and a 480 cm⁻¹ mode in the lower state. Thus, a common upper electronic state was suggested.²³

A vibrational frequency of $\sim \! 310~cm^{-1}$ in an excited state of the emitting species differs from the excited state vibrational values of $\rm Si_3$ in a neon matrix (Table 2). Furthermore, the spectral region of the emission spectrum does not overlap with the absorptions observed in the neon matrix with mass-selected $\rm Si_3$. Thus, the emitting states are probably not singlet states of $\rm Si_3$.

D. Si_3^- . Codeposition of mass-selected Si_3^- with neon results in the appearance of an intense band system in the near infrared (Figure 4). It consists of a series of narrow absorption peaks with a multiplet structure. The spectrum disappears on irradiating the matrix with UV light from a mercury lamp. This is accompanied by the appearance of absorptions characteristic of neutral Si_3 . The spectrum in Figure 4 is consequently assigned to an electronic transition of Si_3^- .

By using a series of optical filters, it was observed that the absorption spectrum of $\mathrm{Si_3}^-$ begins to diminish in intensity on irradiation at $\lambda \approx 420$ nm. The system disappears entirely at $\lambda \approx 365$ nm. This indicates that the detachment energy of $\mathrm{Si_3}^-$ in a neon matrix is in the 2.95–3.4 eV range. The gas phase electron affinity of $\mathrm{Si_3}$ is 2.33 eV.15

Ab initio calculations for $\mathrm{Si_3}^-(C_{2\nu})$ at the QCISD(T)/6-31G* level show that the ground state is X $^2\mathrm{A_1}$.⁴⁰ Another calculation of excited state energies for $\mathrm{Si_3}^-$ made with the CASMP2/ [5s4p2d] method predicts that the lowest excited state, also of $^2\mathrm{A_1}$ symmetry, lies 1.24 eV above the ground state.⁴¹ This is

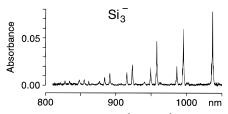


Figure 4. Absorption spectrum of the ${}^{2}A_{1} \leftarrow X {}^{2}A_{1}$ electronic transition of Si₃⁻ in a 5 K neon matrix. The spectrum was measured after mass-selected Si₃⁻ ions were codeposited with excess of neon.

TABLE 3: Observed Band Maxima of the ${}^2A_1 \leftarrow X \, {}^2A_1$ Electronic Transition of Si_3^- ($C_{2\nu}$ Symmetry) in a 5 K Neon Matrix

$\lambda (\text{nm})^a$	$\nu (\mathrm{cm}^{-1})^b$	$\Delta \nu \ (\mathrm{cm}^{-1})$	assignment
1036.7	9 946	0	${}^{2}A_{1} \leftarrow X {}^{2}A_{1} 0_{0}^{0}$
995.7	10 043	397	2_0^1
986.4	10 138	492	10
958.1	10 437	791	$1_0^{\tilde{1}}$ 2_0^2
949.6	10 531	885	$1_0^{1} 2_0^{1}$
940.9	10 628	982	1_0^2
923.5	10 828	1182	$1_0^{1} 2_0^{1}$ 1_0^{2} 2_0^{3} $1_0^{1} 2_0^{2}$
915.6	10 922	1276	$1_0^{1} 2_0^{2}$
907.5	11 019	1373	$1_0^{\frac{1}{2}} 2_0^{\frac{1}{1}}$
891.6	11 216	1570	2_0^4
884.2	11 310	1664	$1_0^1 2_0^3$
876.8	11 405	1759	$1_0^2 2_0^2$ 2_0^5
861.7	11 605	1959	2_0^5
855.1	11 695	2049	$1_0^1 2_0^4$
848.2	11 790	2144	$1_0^2 2_0^3$
834.2	11988	2342	2_0^6
827.8	12 080	2434	$1_0^{1} 2_0^{5}$
821.3	12 176	2530	$1_0^{\frac{3}{2}} 2_0^{\frac{4}{4}}$
			0 0

 $^{^{}a}\pm0.2$ nm. b The uncertainty can be derived from the first column.

in agreement with the energy of the 0_0^0 transition (1.20 eV) and thus the band system is assigned to the ${}^2A_1 \leftarrow X {}^2A_1$ transition of Si_2^-

The positions of absorption peaks observed in the electronic spectrum of Si_3^- are listed in Table 3, where a vibrational assignment is given. The excitation of two vibrational modes, ν_1 and ν_2 , is apparent as well as their combination bands. From the position of the 18 bands, the values $\omega_1=495$ and $\omega_2=402$ cm⁻¹ were evaluated for the $^2\mathrm{A}_1$ excited state of Si_3^- . The inferred anharmonicity constants x_{11} , x_{12} , and x_{22} are too small, 1-4 cm⁻¹, to be deemed significant because of the uncertainty (± 2 cm⁻¹) of the band maxima in the matrix. Vibrational frequencies have been calculated for Si_3^- only in the ground state: $\nu_1=533$ cm⁻¹ and $\nu_2=297$ cm⁻¹.⁴⁰

E. Si₄. Matrix isolation of mass-selected Si_4^- under continuous irradiation of the matrix with UV light leads to the observation of two intense absorption band systems. One is in the 790–930 nm (Figure 5) and the other in the 410–470 nm (Figure 6) region. These systems are associated with electronic transitions of Si_4 .

1. 790–930 nm System. This band system is characteristic of a transition with a considerable geometry change as indicated by the Franck–Condon profile. A vibration with frequency of \sim 304 cm⁻¹ is excited. Each band comprises multiplet site structure. The wavelengths of the absorption bands are given in Table 4.

The photoelectron spectrum of Si₄⁻ consists of four bands at energies 0.81, 1.45, and 2.01 eV above that of the ground state. ¹⁵ In a ZEKE spectrum of Si₄⁻ the band at 1.45 eV is not observed, but a weak band lying 1.37 eV above the ground state is

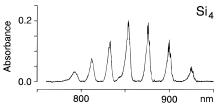


Figure 5. ${}^{1}B_{3u} \leftarrow X {}^{1}A_{g}$ electronic transition of Si₄ recorded after massselection of Si₄⁻ and codeposition with excess of neon at 5 K. The surface of the matrix was exposed to UV light during deposition.

TABLE 4: Band Maxima of the Observed ${}^{1}B_{3u} \leftarrow X {}^{1}A_{g}$ and ${}^{1}B_{1u} \leftarrow X {}^{1}A_{g}$ Electronic Transition of Si₄ and Proposed Assignment (D_{2h} Symmetry) in a 5 K Neon Matrix

issignment	(D 2n Symmetr	y) in a S ix rico	n matrix
$\lambda (\text{nm})^a$	$\nu (\mathrm{cm}^{-1})^b$	$\Delta v \text{ (cm}^{-1}\text{)}$	assignment
927.2	10 785		site
926.6	10 792		site
925.3	10 807	0	${}^{1}B_{3u} \leftarrow X {}^{1}A_{g} 0_{0}^{0}$
924.3	10 819	214	site
907.3	11 022	214	60
900.0	11 111	304	$\begin{array}{c} 6_0^2 \\ 2_0^1 \\ 2_0^1 6_0^2 \\ 2_0^2 6_0^2 \\ 2_0^2 6_0^2 \\ 2_0^3 \\ 2_0^4 \\ 2_0^5 \end{array}$
883.2	11 322	515	$2_0^1 6_0^2$
876.3	11 412	604	2_0^2
860.5	11 621	814	$2_0^2 6_0^2$
854.0	11 710	902	2_0^3
833.1	12 003	1196	2_0^4
812.3	12 311	1503	2_0^5
793.1	12 609	1801	2_0^{6}
466.6	21 432	0	${}^{1}B_{1u} \leftarrow X {}^{1}A_{g} 0_{0}^{0}$
465.7	21 473	41	site
459.8	21 749	317	2_0^1
457.4	21 863	431	1_0^1
453.4	22 056	624	2_0^2
451.0	22 173	741	$1_0^1 2_0^1$
448.7	22 287	855	1_0^2
447.2	22 361	930	2_0^3
444.7	22 487	1055	$1_0^1 2_0^2$
442.4	22 604	1172	$1_0^2 2_0^1$
441.1	22 671	1239	$2_0^4, 1_0^3$
438.7	22 795	1363	$1_0^1 2_0^3$
436.5	22 910	1478	$1_0^2 2_0^2$
435.2	22 978	1546	2_0^{5}
434.4	23 020	1589	$\begin{array}{c} 2_0^1 \\ 1_0^1 \\ 2_0^2 \\ 1_0^1 \\ 2_0^2 \\ 1_0^1 \\ 2_0^1 \\ 2_0^2 \\ 1_0^1 \\ 2_0^2 \\ 2_0^1 \\ 1_0^2 \\ 2_0^1 \\ 1_0^2 \\ 2_0^2 \\ 2_0^2 \\ 2_0^2 \\ 1_0^3 \\ 2_0^1 \\ 2_0^2 \\ 2_0^2 \\ 2_0^3 \\ 1_0^3 \\ 2_0^1 \end{array}$
432.9	23 100	1668	$1_0^{1} 2^{0}$
430.7	23 218	1786	$1_0^{\frac{3}{2}} 2_0^{\frac{3}{2}}$
429.4	23 288	1857	2_0^6
428.6	23 332	1900	$1_0^3 2_0^4$
427.2	23 408	1977	$1_0^1 2_0^5$
424.9	23 535	2103	$1_0^2 2_0^4$
422.8	23 652	2220	$1_0^3 2_0^3$
421.6	23 719	2288	$1_0^1 2_0^6$
419.5	23 838	2406	$1_0^2 2_0^5$
417.4	23 958	2526	$1_{0}^{1} 2_{0}^{0}$ $1_{0}^{2} 2_{0}^{3}$ 2_{0}^{6} $1_{0}^{3} 2_{0}^{4}$ $1_{0}^{1} 2_{0}^{5}$ $1_{0}^{2} 2_{0}^{4}$ $1_{0}^{1} 2_{0}^{3}$ $1_{0}^{1} 2_{0}^{6}$ $1_{0}^{2} 2_{0}^{5}$ $1_{0}^{3} 2_{0}^{4}$ $1_{0}^{3} 2_{0}^{4}$

 $^{^{}a}$ ± 0.2 nm. b The uncertainty can be derived from the first column.

present.¹⁷ These photoelectron spectra were assigned on the basis of *ab initio* calculations and by considering the differences in selection rules between the two techniques.⁴⁰ The calculations indicate that Si₄ has a rhombic structure (D_{2h} symmetry) with a $^{1}A_{g}$ electronic ground state $^{40,42-44}$ and that the bands observed can be assigned to the X $^{1}A_{g}$, a $^{3}B_{3u}$, B $^{1}B_{3u}$, b $^{3}B_{g}$, and d $^{3}B_{1u}$ electronic states of Si₄.^{17,40}

Among these excited electronic states of Si_4 the only allowed electronic transition from the ground state is to $^1B_{3u}$. This state lies 1.37 eV above the ground state, in agreement with the

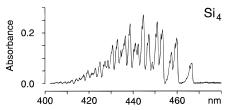


Figure 6. Absorption spectrum of the ${}^{1}B_{1u} \leftarrow X {}^{1}A_{g}$ electronic transition of Si₄. It was measured after codeposition of mass-selected Si₄⁻ and excess of neon under simultaneous irradiation with UV light.

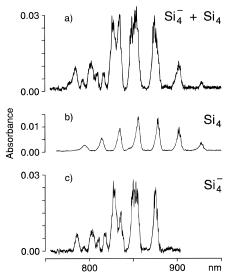


Figure 7. Trace a shows the absorption spectrum measured after deposition of mass-selected Si_4^- together with excess of neon. By subtracting the spectrum of the ${}^1B_{3u} \leftarrow X \, {}^1A_g$ electronic transition of Si_4 (trace b) the ${}^2B_{1u} \leftarrow X \, {}^2B_{2g}$ electronic transition of Si_4^- in a neon matrix remains (trace c).

 0_0^0 energy (1.34 eV) of the transition seen in Figure 5. Furthermore, the frequency of 300 ± 6 cm⁻¹ for the vibration which gives rise to the progression in the ZEKE spectrum of this state (B $^1B_{3u}$) agrees with the 304 ± 4 cm⁻¹ value inferred from the absorption spectrum. On the basis of this we assign the band system in Figure 5 to the $^1B_{3u} \leftarrow X$ 1A_g electronic transition of Si_4 .

The low intensity of the 0_0^0 band and the long progression in the 304 cm⁻¹ mode (ν_2 , a_{1g}) in the absorption spectrum are associated with a change in geometry in the $^1B_{3u}$ excited electronic state. This is also indicated by the change of the ν_2 frequency in the $^1B_{3u}$ (304 cm⁻¹) state compared to 345 cm⁻¹ in the 1A_g ground state.⁴⁵ The latter has been determined by Raman spectroscopy of mass-selected silicon clusters codeposited with N_2 on a 15 K substrate.

2. 410–470 nm System. The system consists of a series of bands with doublet structure, separated by \sim 40 cm⁻¹ (Figure 6). The positions of the absorption bands and their assignments are given in Table 4. A vibrational analysis shows the excitation of two totally symmetric modes of frequencies 317 \pm 14 and 431 \pm 14 cm⁻¹ as progressions and combination series.

Even though QCISD(T)/[7s6p3d1f] *ab initio* calculations⁴⁰ provide a good description of the photoelectron spectrum of Si₄⁻ (which consists mainly of transitions to triplet states of Si₄), they overestimate the energies of singlet excited states of Si₄. These place the state ¹B_{3u} 1.89 eV above the ground state, 0.55 eV above the energy determined from the absorption spectrum of Si₄. The next higher singlet state, ¹B_{1u}, to which a transition from the ¹A_g ground state is dipole allowed, is according to the calculations 3.26 eV above the ground state.⁴⁰ On the expectation that its energy is overestimated by a similar

TABLE 5: Maxima of the Observed Bands in the ${}^2B_{1u} \leftarrow X \, {}^2B_{2g}$ Electronic Transition of $Si_4^- (D_{2h} \text{ Symmetry})$ in a 5 K Neon Matrix

$\lambda (\mathrm{nm})^a$	$\nu (\mathrm{cm}^{-1})^b$	$\Delta v \text{ (cm}^{-1}\text{)}$	assignment
872.6	11 460	0	${}^{2}B_{1u} \leftarrow X {}^{2}B_{2g} 0_{0}^{0}$
851.9	11 738	278	2_0^1
846.6	11 812	352	$1_0^{\tilde{1}}$
833.1	12 003	543	2_0°
826.0	12 107	647	$1_0^{1} 2_0^{1}$
824.0	12 136	676	1_0^2
815.4	12 264	804	2_0^{3}
807.8	12 379	919	$1_0^{1} 2_0^{2}$
802.2	12 466	1006	1_0^3
799.3	12 511	1051	2_0^4
791.3	12 637	1177	$1_0^{1} 2_0^{3}$
784.1	12 753	1293	2_0^5
782.0	12 788	1328	1_0^{4}

 $^{a}\pm0.2$ nm. b The uncertainty can be derived from the first column.

amount to that for the ${}^{1}B_{3u}$ state, an excitation energy of 2.71 eV is obtained. This is close to the energy of the 0_{0}^{0} band (2.66 eV) in the spectrum of Figure 6. It is therefore assigned to the ${}^{1}B_{1u} \leftarrow X {}^{1}A_{g}$ electronic transition of Si₄. This excited electronic state was energetically not accessible in the photoelectron spectrum of Si₄ $^{-}$.15

In the 420–470 nm spectral region a number of weak absorption bands were observed in earlier experiments on matrix isolation of silicon vapor but were tentatively assigned to $\mathrm{Si_3}^{20}$. The positions of these peaks are close to those presently observed (Table 4). Also the gas phase emission spectrum of a silicon plasma in the 420–450 nm region²³ partially overlaps with the $^{1}\mathrm{B_{1u}} \leftarrow \mathrm{X}^{-1}\mathrm{A_g}$ transition of $\mathrm{Si_4}$. The vibrational frequency of 310 cm⁻¹ determined from the emission spectrum is in fact close to that found here for the $^{1}\mathrm{B_{1u}}$ state of $\mathrm{Si_4}$.

F. Si_4^- . On forming a neon matrix with mass-selected Si_4^- anions a band system is detected in the 750–950 nm range (Figure 7a). This lies in the same region as the $^1B_{3u} \leftarrow X$ 1A_g transition of Si_4 , 15 and in fact weak peaks to the red are those of Si_4 (Figure 7b). On subtracting the two spectra the absorption shown in Figure 7c is obtained. This consists of a series of peaks with multiplet structure. These disappear on irradiation with UV light and, in the process, the two band systems of the neutral molecule Si_4 increase in intensity. On this basis we attribute the band system in Figure 7c to Si_4^- . The positions of the peaks together with a proposed vibrational assignment of $\nu_1 = 352 \pm 4$ cm⁻¹ and $\nu_2 = 278 \pm 4$ cm⁻¹ are given in Table 5.

Ab initio calculations predict that the ground state of $\mathrm{Si_4}^-$ is ${}^2\mathrm{B}_{2\mathrm{g}}$ (rhombic D_{2h}). 40,46 Of the calculated excited states (coupled cluster method) the only allowed transition is to a ${}^2\mathrm{B}_{1\mathrm{u}}$ state. The latter is predicted to lie 1.44 eV above the ground state, in good agreement with the energy determined from the present spectrum (0^0_0 transition at 1.42 eV). Therefore, the observed absorption spectrum is assigned to the ${}^2\mathrm{B}_{1\mathrm{u}} \leftarrow \mathrm{X} \, {}^2\mathrm{B}_{2\mathrm{g}}$ electronic transition of $\mathrm{Si_4}^-$.

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