Photoelectron spectroscopy of C_3Si and C_4Si_2 anions

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The 364 nm photoelectron spectra of the linear C_3Si^- and $C_4Si_2^-$ anions are reported. Accurate adiabatic electron affinities are determined: $EA(^3\Sigma\ C_3Si) = 2.827 \pm 0.007$ eV and $EA(C_4Si_2) = 2.543 \pm 0.006$ eV. Several vibrational frequencies for both neutral molecules are also obtained. The term energy for the first linear excited state of C_3Si (either $^1\Delta$ or $^1\Sigma$) is 0.274 ± 0.015 eV. For C_4Si_2, the term energy is substantially lower than in C_3Si and vibronic interactions between the two states become stronger. Experimental results are compared with high-level *ab initio* calculations for C_3Si (see Rintelman and Gordon, following paper) and with our own calculations for C_4Si_2 and its anion. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1380713]

I. INTRODUCTION

A more complete understanding of the reactivity and electronic properties of silicon carbide and oxygenated silicon carbide surfaces at high temperatures is a subject of current fundamental and applied interest. Our group addresses this issue through the study[1,2] of small, mass-selected silicon carbide cluster anions. Photoelectron spectroscopy of these anions gives information on the electron affinity as well as the neutral electronic state ordering at the geometry of the anion; these data provide a very useful guide for electronic structure calculations of finite SiC clusters. It is this aspect that motivates the present collaboration involving our experimental investigations and high-level electronic structure calculations of small SiC clusters.[3,4] From the point of view of basic chemistry, these clusters are of interest because silicon and carbon belong to the same group in the periodic table, but have dramatically different bonding properties. The difference is due to the tendency of carbon to form higher order bonds while silicon tends to form multidirectional single bonds. These properties contribute to substantial differences between the geometries of large silicon and carbon clusters. Silicon carbide clusters have also been of interest because of their astrophysical importance. Cyclic SiC_2 and SiC_3 and linear SiC_4 have been detected in circumstellar media.[5–7]

There has been a great deal of interest in silicon–carbon clusters throughout the past decade. Both *ab initio* calculations and anion photoelectron spectroscopy experiments have been used to look at many different clusters of varying size and composition. Pure silicon (Si_n, $n = 3 – 7$) and carbon (C_m, $m = 2 – 11$) clusters have been extensively studied via anion photoelectron spectroscopy experiments.[8–11] While most studies on mixed Si_nC_m clusters have focused on one or two specific clusters, there has been some work that has looked at a large group of clusters. Nakajima *et al.* reported an extensive study of various $Si_nC_m^-$ anions using photoelectron spectroscopy.[12] Vertical detachment energies (VDEs)

were reported, but the adiabatic electron affinities could only be estimated, due to limited instrument resolution.

Calculations by Hunsicker and Jones[13] focused on the same group of clusters, obtaining VDEs, geometries, frequencies, and energetics of different isomers for both the anion and neutral species. Their results were in agreement with the experimental results of Nakajima *et al.*[12] Two additional studies from the Kaya group calculated various parameters for the Si_nC and SiC_m species.[14,15] A number of calculations have also been performed on the $n + m = 4 – 6$ clusters at various levels of theory.[13–18] These studies have predicted geometries, frequencies, energies, and, in some cases, IR intensities.

The difficulty of such calculations is well exemplified by an examination of the conclusions for one of the smaller clusters, C_3Si. The ground state C_3Si surface exhibits multiple low-lying minima, and both their relative energies and the identity of the **global** minimum have been found to be strongly dependent on the basis set and theoretical method employed. There is general agreement that the two lowest-lying states are a singlet rhombic structure (C_{2v}) and a triplet form. Nakajima *et al.* report calculations showing the rhombic form to be the lowest in energy by 0.3 eV.[15] Other calculations by Hunsicker and Jones[13] find these two states to be nearly degenerate, with the linear state form lying 0.01 eV higher. An earlier study found that the rhombic geometry is more stable by only 0.18 eV.[16] However, Rintelman and Gordon[4] have undertaken high level *ab initio* calculations on these two states, and their results indicate that the ground state of C_3Si is in fact the linear $^3\Sigma^-$ state, and the $^1A_1$ rhombic state lies 4.4 kcal/mole above the linear configuration. This investigation[4] provides the clearest computational evidence to date concerning the global minimum, and indicates that the linear geometry with a terminal Si atom is the global minimum. Even that calculation, however, does not yield clearly converged energies for the low-lying **excited** states of C_3Si. Further complication is added when it is appreciated that the only experimental observations of C_3Si have been of the rhombic configuration.[5,19–21] There is a substantial body of astronomical observational data for C_3Si;

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many rotational transitions have been observed.[5] Subsequent laboratory work has investigated C_3Si in a supersonic expansion with a Fourier transform microwave spectrometer and in a low pressure dc glow discharge with a free space millimeter-wave absorption spectrometer.[19–21] The fact that only the cyclic form has been observed experimentally could be taken as an argument that the cyclic form is lowest in energy.

In this paper, we report the photoelectron spectra of several C_nSi_m anions with the $n+m=$ even structure, C_3Si^- and $C_4Si_2^-$. The anions are expected to be linear, with terminal Si atom(s). In analogy with silicon and carbon clusters, these species are expected to have electron affinities greater than the neighboring $n+m=$ odd species. Several properties of the neutral were obtained, including adiabatic electron affinities, a few vibrational frequencies, and term energies for the first excited electronic states. We also observed $C_6Si_2^-$ in the mass spectrum; however, the ion beam intensity and the complexity of the spectrum prevented us from obtaining a useful spectrum for this species.

II. EXPERIMENT

The details of the negative ion photoelectron spectrometer and the general experimental procedure have been described previously,[2] only a brief overview is given here. Several C_mSi_n anions are synthesized in a flowing afterglow apparatus by the use of a cold cathode discharge. The anion source has been described in detail previously.[22,23] Briefly, it operates by sputtering clusters from a cathode with a dc discharge in a flowing afterglow source with a mixture of 10–15 % of argon in a helium buffer gas. The C_mSi_n anions are produced when Ar^+ is accelerated towards the negatively biased cathode, a silicon carbide rod (Goodfellow) that is 50 mm in length by 5 mm in diameter. The typical cathode voltage is 2300 V with respect to the grounded flow tube. Currents of a few picoamperes of mass selected anions were produced during our experiments and were very dependent on the ion stoichiometry and flow tube temperature. In room temperature experiments, the ions have a vibrational temperature of ~300 K following collisional relaxation with the buffer gas. Whenever possible, spectra were also collected with the flow tube cooled by liquid nitrogen, which lowers the vibrational temperature to approximately 180 K.

Upon extraction from the flowing afterglow tube, ions are accelerated to 735 eV into a low-pressure region and mass selected by a Wien velocity filter. The mass selected beam is further focused and then decelerated to 38 eV prior to entering the laser interaction region where the ion beam is crossed with the 364 nm line of an argon ion laser in a build-up cavity with ~100 W of circulating power. Photoelectrons ejected into a small solid angle perpendicular to the ion and laser beam are focussed into a hemispherical energy analyzer and detected by a position sensitive detector with an overall resolution of ~10 meV. Energies of transitions between the anion and the corresponding neutral are determined from the difference between the photon energy (3.408 14 eV) and the measured electron kinetic energy. The absolute energy scale is calibrated by the position of the
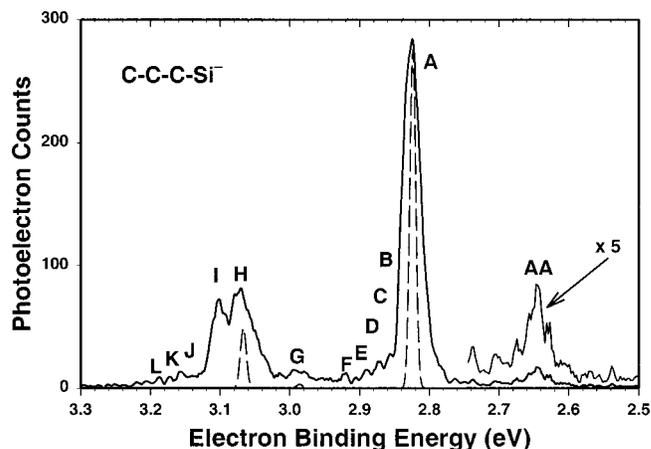

FIG. 1. The 364 nm photoelectron spectrum of C_3Si^- taken at room temperature (solid line). The simulated spectrum for the $^3\Sigma^-$ ground state calculated at the MP2/aug-cc-pVDZ level and by using a Franck–Condon routine is also plotted (dashed line).

$^3P_2 \leftarrow {}^2P_{3/2}$ transition in the O^- spectrum.[24] The apertureless nature of the analyzer allows for the possibility of a small electron energy scale compression. This compression factor (~1%) is obtained by measuring the positions of six well-known transitions in the W^- photoelectron spectrum.[25]

A half-wave plate placed just before entrance to the build-up cavity can rotate the laser polarization, allowing determination of photoelectron angular distributions.[2] Unless otherwise noted, all spectra are recorded with the laser polarization oriented at the magic angle (54.7°) relative to the electron detection direction, such that photoelectron signal is independent of the angular distribution.[26] To determine the asymmetry parameter (β), spectra are collected with the laser polarization parallel (0°) and perpendicular (90°) to the photoelectron collection direction, using the expression

$$\beta = \frac{I_0 - I_{90}}{\frac{1}{2}I_0 + I_{90}},$$

where I_0 and I_{90} are the peak intensities taken at 0° and 90°, respectively.[26]

Ab initio calculations were carried out for the electronic ground states of the anions and the ground and first excited electronic states in the neutral species using the GAUSSIAN 98 suite of programs.[27] Geometry optimizations and frequency calculations were performed at the MP2/aug-cc-pVDZ level for C_3Si, while the hybrid density functional theory (DFT) method B3LYP with the aug-cc-pVDZ basis set was used for C_4Si_2. A slightly modified version of the Franck–Condon program CDECK was used to determine the spectra based upon the calculated anion and neutral geometries and harmonic vibrational frequencies.[28]

III. RESULTS AND DISCUSSION

A. C_3Si

1. Spectra and assignment

The 364 nm photoelectron spectrum of C_3Si^- obtained at the magic angle orientation is displayed in Fig. 1. The ~3 pA C_3Si^- current diminished further upon cooling the flow

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tube, and we were unable to obtain a useful cooled ion photoelectron spectrum. The spectrum shows three intense features (peaks A, H, and I) and two sequences of weak transitions (each spaced ~ 130 cm^{-1}) built off of intense peaks A and I. In addition, there is also a very small feature at low binding energies that we attribute to a transition from a different isomer of C_3Si^-. The general shape of the spectrum suggests that the detachment occurs with little change in geometry, as indicated by the lack of extended vibrational progressions. Moreover, the spectrum shown in Fig. 1 is very similar to that reported[9] for the linear C_4^- anion, suggesting that C_3Si^- is also linear, in accord with calculations.[12,13,15] Thus peak A is assigned as the 0–0 transition from the linear anion to the linear ground state of C_3Si, yielding EA(C_3Si)=2.827±0.007 eV, in agreement with the VDE of 2.86 eV and the 2.81 eV adiabatic electron affinity, as calculated by Hunsicker et $al.$[13] and Gomei et $al.$[15]

2. Analysis

As with the analogous C_4^- anion, linear C_3Si^- is expected to have a π^3 $^2\Pi$ valence electron configuration. This configuration is also supported by our own and several other ab $initio$ calculations.[13,15,16,29] Detaching a valence electron generates $^1\Sigma^+$ (detaching the unpaired electron), $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ states. Since all of these states arise from detaching an electron of the same orbital symmetry, the photoelectron angular distributions will be similar for all of these transitions and cannot be used to identify the final states. The photoelectron angular distributions observed for all intense transitions exhibited an anisotropy parameter β of -0.6, consistent with detaching a π electron from C_3Si^-. With this information we can utilize our single determinant ab $initio$ structure and frequency calculations for the $^2\Pi$ anion and the $^3\Sigma^-$ neutral to simulate the photoelectron spectrum, providing a rigorous test of the assignments. This simulation agrees very well with the experiment, with respect to both the vibrational frequencies of the neutral that are observed upon electron detachment and their intensity, the latter being a test of the magnitude and nature of the geometry changes upon electron detachment. Peaks G and H arise from transitions to vibrational modes with frequencies of 1320 ± 20 and 1980 ± 20 cm^{-1}, respectively (see Table I). These observed values correspond very closely to the frequencies of the totally symmetric 1,3 C–C stretch and C–C stretch modes calculated by Rintelman and Gordon[4] for the $^3\Sigma^-$ state. The only other totally symmetric (σ) mode, a Si–C stretch, shows little geometry change upon electron detachment and indeed is not observed in the photoelectron spectrum. Thus the major features in the spectrum are in complete accord with linear anion and neutral geometries.

As seen in Fig. 1, there is also a progression of weak peaks (B–F), transitions to the high binding energy side of peak A, spaced by ~ 130 cm^{-1}. These peaks arise from transitions to nontotally symmetric (π symmetry, bending) vibrational modes, transitions forbidden in the Franck–Condon approximation and thus absent in our simulated spectrum. Similar transitions were observed in the carbon C_{2n}^- photoelectron spectra, and Neumark proposed that they obtained intensity from mixing with a low-lying electronic state of the

TABLE I. Peak positions and assignment for the C_3Si^- photoelectron spectrum.

Peak	Binding energy eV	Splitting from origin (cm^{-1})	Assignment
AA	2.629	−1600	Transition between nonlinear isomers of C_3Si (see text)
A	2.827	0	$^3\Sigma^-$ 0_0^0
B	2.856	230	5_0^2
C	2.872	370	5_0^3
D	2.890	510	5_0^4
E	2.905	630	5_0^5
F	2.921	760	5_0^6
G	2.990	1320	2_0^1
H	3.072	1980	1_0^1
I	3.101	0	$^1\Delta$ or $^1\Sigma^+$ 0_0^0
J	3.156	440	5_0^3
K	3.172	575	5_0^4
L	3.188	703	5_0^5

same Π symmetry.[9] While this mixing is almost surely present, this mode can also gain intensity from the small Renner–Teller effect present in the anion.[30] The experimental frequency of this skeletal bending mode is 135 ± 25 cm^{-1}, in agreement with the 130 cm^{-1} frequency calculated by us and by several others.[4,13,15,16] The assignments for these transitions are summarized in Table I.

Several other observations also argue strongly in favor of the linear configuration. Among the low-lying geometries corresponding to local minima, only the linear configuration has **any** vibrational frequency calculated to be less than 250 cm^{-1}. The two observed totally symmetric vibrational frequencies are in excellent agreement with those calculated for the linear SiC_3 neutral, and they are very difficult to reconcile with other geometries. Specifically, the observed high frequency C–C stretch (1980 cm^{-1}) agrees with that calculated by Alberts et $al.$[16] (2037 cm^{-1}), Gomei et $al.$[15] (2003 cm^{-1}), and with the elaborate calculation of Rintelman and Gordon[4] (2003 cm^{-1}). None of the calculations for the rhombic forms predicts[4,15,16] a vibrational frequency that is nearly this large.

Additional support for the linear configuration comes from electron affinity calculations carried out by Gomei et $al.$[15] at the CCSD(T)/aug-cc-pVTZ level. They predict the electron affinity of the linear form to be 2.81 eV and that of the rhombic form to be 1.88 eV. Our 2.827 eV experimental determination is in much better agreement with a linear form. Given that both vibrational frequencies and electron affinity calculated for the linear form agree well with observations, and similar calculations for the rhombic form do not agree, the assertion that the observed transitions arise from a linear anion is likely correct.

Having assigned peaks A to H, it is clear from Fig. 1 that peak I is the 0–0 transition to the first excited state of linear C_3Si, lying ~ 6.3 kcal/mol above the ground state. Both $^1\Delta$ and $^1\Sigma$ states are expected to be low-lying, and transitions to either state should exhibit intensity comparable to the ground state transition. While a first expectation is that the $^1\Delta$ state

should be the lower, our experiments cannot distinguish between these alternatives; indeed the broadness of this peak and the lack of full vibrational assignments means that "peak *I*" could even represent two nearly degenerate electronic states. Calculations have not yet provided a firm identification of this transition. Employing a 6-31G(d) basis set, Rintelman and Gordon[4] calculate the $^1\Delta$ state to lie 6.6 kcal/mol above the $^3\Sigma^-$ ground state, and the $^1\Sigma^+$ state to lie 10 kcal/mol above the ground state. This result agrees well with our measured 6.3 kcal/mol excitation energy and argues for a $^1\Delta$ assignment for peak *I*. However, Rintelman and Gordon carried out additional calculations with an aug-cc-pVDZ basis set, primarily because they could then employ a consistent basis set for both anion and neutral species. While the addition of diffuse functions might not be expected to make a substantial difference in the neutral state energies, these latter calculations[4] show the $^1\Sigma^+$ and $^1\Delta$ states lying 9.3 and 10.6 kcal/mole above the ground state, respectively. It appears that the excited state calculations are not yet sufficiently well converged to assist in the identification of the electronic state associated with peak *I*. In any event, peaks *J*–*L* are similar to peaks *B*–*F* in the ground state, corresponding to transitions to nontotally symmetric (bending) vibrational modes within this state, with a frequency of 140 ± 25 cm^{-1} (Table I).

3. Anion isomers

The presence of a low-lying electronic excited state of C_3Si^- is suggested by the presence of the weak peak *AA* in the spectrum seen in Fig. 1, especially when combined with the C_3Si^- observations of the Kaya group.[12] They employed a laser ablation ion source, one that could readily be expected to initially produce more excited anions than our high pressure sputter ion source. They report[12] a weak, broad structureless band in the C_3Si^- photoelectron spectrum, extending from an electron binding energy of ~1.7 eV up to the intense feature (peak *A*) reported here. They show[12] that the intensity of this broad feature depends upon ion source conditions and corresponds to an anion that is **less stable** than the linear anion. They attribute this band to transitions from a planar ring form of the anion (a $^2B_1$ state calculated[12,15] to lie ~0.6 eV above the linear form) to the corresponding $^1A_1$ state of the neutral. It is possible that the weak peak *AA* that we observe at a binding energy of ~2.63 eV arises from a vibrationally cooler $^2B_1$ cyclic anion. While some low-frequency vibrational modes appear to be present, the quality of the spectrum discourages an analysis more detailed than a report of the binding energy corresponding to peak *AA*, and attributing it to a ring–ring transition.

The binding energy of the major feature attributed to the linear state reported by Nakajima *et al.*[12] agrees well with our results. The binding energy that we obtain for the ring form (2.63 eV) is considerably higher than that reported by Nakajima,[12] but they observe a very broad, flat, weak feature extending from 1.7 eV to 2.8 eV, with no clearly assignable components. However, close inspection of the broad feature in their spectrum shows what may possibly be the peak *AA* that we observe. This may be the electron affinity transition in their broad feature, or it may be that a third isomer of
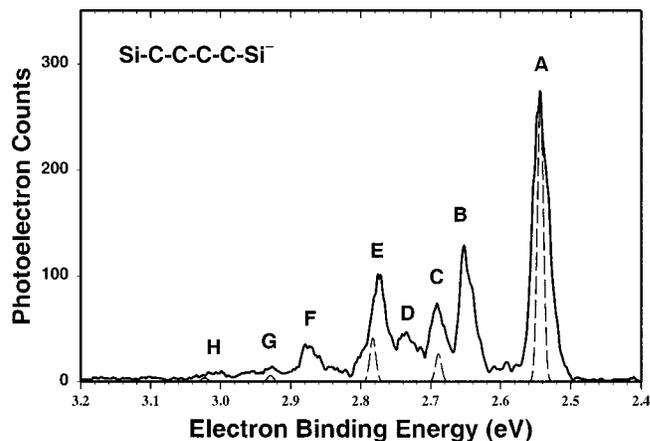

FIG. 2. The 364 nm photoelectron spectrum of $C_4Si_2^-$ taken at 180 K (solid line). The calculated spectrum for the $^3\Sigma^-$ ground state is shown as a dotted line.

C_3Si^- has been identified. Our experiments cannot resolve this issue.

The 2.63 eV adiabatic detachment energy that we observe for the ring form is plausible, given that Gomei's calculations suggest that the ring anion lies ~0.6 eV **above** the linear anion[15] and the new calculations by Rintelman and Gordon[4] place the cyclic neutral about 0.2 eV above the linear form. Since the 2.827 eV electron affinity of the linear form is unambiguous, these values would predict a value of ~2.5 eV for an adiabatic detachment energy of the cyclic form of C_3Si, comparable to the 2.63 eV determined as the binding energy of the most intense component of peak *AA*. We cannot claim this value to be the adiabatic detachment energy with certainty, but it is definitely the vertical detachment energy (VDE) for this form of the anion. There appears to be a vibrational progression with a frequency of ~300 cm^{-1} built off of peak *AA*, but this information, even coupled with the accompanying neutral calculations,[4] is not sufficient to definitively identify the isomer associated with peak *AA*. Clearly, high level *ab initio* calculations on the anion structures will be necessary to assign definitively the origin of the low binding energy spectral feature. In addition, we note that these studies provide no direct information as to whether the linear or cyclic form of C_3Si lies lowest in energy.

B. C_4Si_2

The sputter ion source produced a sufficiently intense beam of $C_4Si_2^-$ so that it was possible to obtain a photoelectron spectrum with the flow tube cooled to 180 K. The resulting magic angle photoelectron spectrum of $C_4Si_2^-$ is depicted in Fig. 2. The spectrum presents a well-resolved progression of peaks (*A*–*H*). The electron affinity is readily assigned to the largest peak, labeled *A*, as 2.543 ± 0.006 eV, in agreement with a calculated vertical detachment energy 2.59 eV.[13] A photoelectron spectrum of this ion has been previously obtained by Nakajima *et al.*,[12] who extrapolate an EA of ~2.38 eV from their less resolved photoelectron spectrum. Table II lists the peak positions of peaks *A*–*H*.

TABLE II. Peak positions and assignment for the $C_4Si_2^-$ photoelectron spectrum.

Peak	Binding energy, eV	Splitting from origin (cm^{-1})	Splitting from excited origin (cm^{-1})	Assignment
A	2.543	0		$^3\Sigma^-(v=0) \leftarrow {}^2\Pi(v=0)$
B	2.652		0	$^1\Delta, {}^1\Sigma^+(v=0) \leftarrow {}^2\Pi(v=0)$
C	2.691	1200		$^3\Sigma^-(v_2=1) \leftarrow {}^2\Pi(v=0)$
D	2.738		695	$^1\Delta, {}^1\Sigma^+(v_5=1) \leftarrow {}^2\Pi(v=0)^a$
E	2.774	1870		$^3\Sigma^-(v_1=1) \leftarrow {}^2\Pi(v=0)$
			990	$+{}^1\Delta, {}^1\Sigma^+(v_2=1) \leftarrow {}^2\Pi(v=0)$
F	2.873		1790	$^1\Delta, {}^1\Sigma^+(v_1=1) \leftarrow {}^2\Pi(v=0)$
G	2.928	3110		$^3\Sigma^-(v_1=1, v_2=1) \leftarrow {}^2\Pi(v=0)$
H	3.005		2850	$^1\Delta, {}^1\Sigma^+(v_1=1, v_2=1) \leftarrow {}^2\Pi(v=0)$

[a]Very tentative assignment. See text for details.

There is considerable evidence that this spectrum arises from photodetachment of a linear, silicon-terminated anion, producing a SiC_4Si neutral. This evidence includes the following: the resemblance of this spectrum to the C_3Si^- spectrum; our own as well as earlier theoretical results;[12,13,31] and data from FTIR studies.[32] Moreover, all this evidence also suggests that the silicon atoms are located at the ends of the chain. This last result should be expected on the basis that silicon atoms do not have the tendency to form multiple bonds, while the carbon atoms do.

All available theoretical results, including our own calculations, predict the ground state of C_4Si_2 to be a linear $^3\Sigma^-$ state. The simulation for this state obtained by using the B3LYP/aug-cc-pVDZ method is also shown in Fig. 2. All vibrational frequencies were scaled by a factor of 0.95, producing good agreement with the two infrared active v_4 and v_5 modes (but inactive in the photoelectron spectrum) at 1807.4 cm^{-1} and 719.1 cm^{-1} detected by Presilla-Marquez and Graham[32] by FTIR. As seen in Fig. 2, the simulation predicts the position and intensity of peaks A, C, and E reasonably well, but other major peaks (B, D, F, and H) are absent from the simulation. There are only three totally symmetric modes in the neutral, and, based upon the calculated geometry changes, we expected to see only the two modes that are observed. Accordingly, we believe that the peaks present in the spectrum but absent from the simulation arise from transitions to a different electronic state. The first missing peak in the simulation is peak B. There is no vibrational mode of any symmetry that can match peak B, the second most intense peak in the spectrum; thus we assign this peak to the 0–0 transition to the lowest linear excited state of C_4Si_2, with a term energy of 0.110 ± 0.004 eV. The nature of the first excited state cannot be established from the experimental data alone. As before, the polarization dependence of the spectra does not help to distinguish between these states, although the data are consistent with detaching an electron from an orbital of π symmetry. As was the case for linear $^3\Sigma^-$ C_3Si, the first linear excited state is expected to be either a $^1\Delta$ or a $^1\Sigma^+$ state. Based upon this assignment, the remaining unassigned peaks (D, F, and H) can be assigned as vibrations associated with the excited state, with frequencies as shown in Table II. The remaining issues for these assignments concern whether the observed frequencies and intensities are compatible with either state. Thus we undertook to model transitions to these states.

We could only calculate the $^1\Sigma^+$ state by using a single determinant wave function; this procedure is clearly incorrect, but it may not be too bad an approximation if all of the states arising from the valence configuration ($^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$) have fairly similar geometries. This approximation was used to obtain vibrational frequencies and geometry changes to simulate the first excited state portion of the spectrum. When peak B was set as the origin, the agreement with peaks E, F, and H is good, especially considering the crudeness of the model for an excited state. The active vibrational modes are the same ones active in the ground state spectrum.

Peak D is the only one that is not predicted by our simulations. Since its position does not match any of the totally symmetric modes in either the ground or excited state, we conclude that it could be either a non-Franck–Condon allowed transition to a 700 cm^{-1} mode of $^3\Sigma^-$ C_4Si_2, or a transition to another excited state C_4Si_2.

Transitions arising from vibronic coupling were observed in the C_3Si^- spectrum (and may also be present in Fig. 2 as the small peaks observed between peaks A and B), but other modes would be expected to be even more intense in the $C_4Si_2^-$ spectrum due to the enhanced vibronic coupling arising as a result of the reduced excited state excitation energy. Recently, we have observed the same kind of interaction in alkoxides.[33] No calculated vibrational frequency in the ground state matches the $A-D$ separation; however, there is a σ_u mode in the first excited state, 690 cm^{-1} (0.95 scaled, as were all other frequencies in this state), that matches the $B-D$ separation, 695 cm^{-1}. Thus, peak D might arise from vibronic coupling producing activity in this mode. However, we cannot exclude the possibility that the transition arises from another excited state. We hope that these results will stimulate high level *ab initio* calculations that will help to discern between these alternatives.

IV. CONCLUSIONS

The photoelectron spectra of C_3Si^- and $C_4Si_2^-$ have been obtained at a resolution of an order magnitude better than reported previously, providing significantly more accurate electron affinities and vibrational frequencies. We observe transitions corresponding to both linear and cyclic forms of C_3Si^-, but the experimental data alone cannot definitively establish whether the global minimum on the C_3Si surface is at the linear or the cyclic configuration.

With the help of high level *ab initio* calculations the term energy for the first excited state (either $^1\Delta$ or $^1\Sigma$) of C_3Si is determined. The energy of the corresponding excited state in C_4Si_2 is considerably less than in C_3Si, and vibronic interactions between the two states are found to be substantially stronger for C_4Si_2.

We also observed $C_6Si_2^-$ in the mass spectrum; however, the low signal combined with the poor detachment cross section and the complexity of the spectrum prevented us from obtaining useful information. We have synthesized several other mixed SiC cluster anions, including CSi_3^-, C_4Si^-, $C_3Si_2^-$, and $C_5Si_2^-$ in our sputter source flow tube; the analysis for those species will be reported shortly. We are also interested in analyzing larger silicon carbide clusters by photoelectron spectroscopy of their negative ions. We are modifying our ion source in order to be able to maximize the intensity of those higher mass clusters, and to synthesize silicon carbide cluster anions with an oxygen adsorbate.

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