Study of Si$_4$ and Si$_4^-$ using threshold photodetachment (ZEKE) spectroscopy

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The threshold photodetachment (ZEKE) spectrum of Si$_4^-$ is presented. Although no transitions to the ground state of Si$_4$ are observed, we obtain detailed information on the anion and several of the low-lying excited states of neutral Si$_4$. The spectrum shows a long progression of well-resolved transitions between the $D_{2g}$ $B_{2g}$ rhombus anion and $v_2$ vibrational levels of the first excited $D_{2h}$ $B_{3h}$ neutral. The length and spacing of the progression is consistent with ab initio calculations performed by Rohlfling and Raghavachari [J. Chem. Phys. 96, 2114 (1992)], but some of the sequence bands observed within the progression are not. We also observe transitions to the Si$_4$ $B_{3u}$ state which is found at a lower excitation energy than predicted. The perturbed vibrational structure in this band is attributed to vibronic coupling to a nearby electronic state which is “dark” with respect to ZEKE spectroscopy. The ZEKE spectra are compared to the previously obtained photoelectron spectra of Si$_4^-$ as well as ab initio calculations on Si$_4^{-}$ and Si$_4$.

I. INTRODUCTION

The study of small silicon clusters has been an area of interest because of their importance in astrophysics and CVD processes. These species are of considerable interest from a purely spectroscopic perspective as well, since ab initio calculations predict dramatic changes in the geometry and bonding in silicon clusters as the number of atoms is varied. However, from an experimental viewpoint, the spectroscopy of silicon clusters is quite poorly characterized with the exception of the dimer, for which several rotationally resolved electronic transitions have been observed. The development of laser vaporization cluster sources has facilitated photofragmentation, photoionization, and “reactive etching” studies, of the larger clusters, but these experiments have revealed little regarding specific cluster structures and bonding. Several absorption lines seen in silicon vapors trapped in rare gas matrices were tentatively attributed to Si$_3$ and Si$_4$, but no analysis of these lines was pursued.

There have been several gas phase spectroscopic studies of silicon clusters with three or more atoms. With the exception of the emission spectroscopy study of Gole and co-workers, in which several transitions from two excited electronic states attributed to Si$_2$ were observed, this work has involved negative ion photodetachment experiments on silicon cluster anions. While the resolution obtained in photodetachment experiments is typically lower than ir absorption techniques, they offer the advantage of mass selection prior to spectroscopic investigation, thereby eliminating any ambiguity concerning species identification. Such experiments have also revealed a great deal about the electronic structure of metal clusters and carbon clusters.

Electronically resolved negative ion photoelectron spectra (PES) of Si$_n^-$ ($n=3$–12) have been obtained by Smalley and co-workers. Higher resolution PES have been measured by Ellison for Si$_2^-$, and by our group for Si$_2^-$–Si$_4$–Si$_6$. These studies have shown that silicon clusters are rich with low-lying electronic states, and the higher resolution studies revealed vibrational structure associated with several of the neutral–anion electronic transitions. We have also studied Si$_3^-$ at even higher resolution using threshold photodetachment (zero electron kinetic energy, ZEKE) spectroscopy. The ZEKE spectrum exhibited fine structure due to spin–orbit splitting both in the anion and neutral dimer, and this proved invaluable in sorting the low-lying electronic states in Si$_3^-$ and Si$_2^-$.

In the case of our Si$_4^-$ and Si$_4^-$ photoelectron spectra, even though vibrational structure is resolved in several of the bands, the assignment of the vibrational and electronic features is greatly facilitated by comparing the experimental spectra to the ab initio work of Raghavachari, Rohlfling, and co-workers. For example, their calculations on Si$_4$ and Si$_4^-$ predicted the ground states to be the $1^1A_g$ and the $3^1B_{2g}$ states, respectively, both of which have planar rhombus ($D_{2h}$) structures. Based on the calculated geometries, which are quite similar, one would expect to see a short progression in the $v_4$ mode of Si$_4$ with a frequency of 357 cm$^{-1}$. This is consistent with the experimental spectra, shown in Fig. 1, thereby supporting the ab initio geometries.

Rohlfling and Raghavachari have also investigated the excited states of Si$_4$ with a rhombus (or near rhombus) equilibrium geometry. They determined that at least six electronic states accessible by detachment of the anion ground state ($3^1B_{2g}$) lie within 2 eV of the neutral ground state, and assigned the three excited state bands in our spectrum (bands A, B, and C) to transitions to the $3^1B_{3u}$, $3^1B_{2g}$, and $3^3B_{1g}$ states of Si$_4$. They also raised the possibility that one of the bands (band B) consisted of overlapping transitions other low lying excited states of Si$_4$. The band assignments according to Ref. 4 are indicated in Fig. 1.

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**FIG. 1.** Photoelectron spectra of \( \text{Si}^-_4 \) (Ref. 17) obtained using 3.493 eV photon energy (top panel) and 4.66 eV photon energy (bottom panel) with the assignments of Rohlfing and Raghavachari (Ref. 4).

The partially resolved vibrational features in Fig. 1 suggest that a higher resolution photodetachment spectrum will reveal considerably more structure. This is the motivation for the work presented here, in which we report the results of threshold photodetachment (ZEKE) spectroscopy on \( \text{Si}^-_4 \). In these experiments, mass-selected anions are photodetached with a tunable laser, and only those electrons with nearly zero kinetic energy are detected. The resolution of our ZEKE spectrometer is around 3 cm\(^{-1}\), considerably better than the photoelectron spectrometer used for Fig. 1 (80–100 cm\(^{-1}\)).

Threshold photodetachment spectroscopy is most powerful when used in tandem with photoelectron spectroscopy. While all neutral–anion electronic transitions involving removal of a single electron can be seen in the photoelectron spectrum of an anion, this is not so for the ZEKE spectrum. According to the Wigner\(^{21}\) threshold law, the photodetachment cross section near the threshold for a neutral–anion transition goes as

\[
\sigma \propto (E_{\text{photons}} - E_{\text{threshold}})^{l+1/2},
\]

where \( l \) is the photoelectron angular momentum. For \( l=0 \) (s wave) detachment, the cross section rises sharply above threshold, but for \( l>1 \) (p wave, etc.) the cross section is very small near threshold. Hence, ZEKE spectroscopy of anions is sensitive only to s wave detachment. While sometimes inconvenient, this feature is often useful in assigning neutral–anion electronic transitions, since s-wave detachment can only result from removal of an electron from particular orbitals.\(^ {22}\) This type of analysis was used in our study of \( \text{Si}^-_2 \) (Ref. 16) as well as in the work presented here.

The \( \text{Si}^-_4 \) threshold photodetachment spectrum shows well resolved bands involving transitions between the \( \text{Si}^-_4 ^2\text{B}_2g \) state and two excited electronic states of neutral \( \text{Si}_4 \). The lower energy band, assigned to the transition to the \( \text{Si}_4 ^3\text{B}_3\text{u} \) state, is particularly clean, and from it we obtain several vibrational frequencies for the anion and neutral which are in partial agreement with the \textit{ab initio} results of Rohlfing and Raghavachari.\(^ {4}\) The higher energy band appears to be strongly perturbed, most likely because of vibronic coupling to an overlapping \( \text{Si}_4 \) excited state which is “dark” with respect to ZEKE spectroscopy. The nature of the electronic states that are involved in this band is discussed in light of the \textit{ab initio} calculations.

**II. EXPERIMENT**

Figure 2 shows a schematic top view of the threshold photodetachment apparatus. It is described in detail elsewhere,\(^ {23} \) but the basic operation is as follows. Cold silicon clusters (anions, cations, and neutrals) are generated in a laser vaporization/pulsed molecular beam source similar to that developed by Smalley.\(^ {24} \) Helium is used as the carrier gas, typically with a backing pressure between 50 and 80 psi. Use of a piezoelectric valve\(^ {25} \) rather than the solenoid-type molecular beam valve (General Valve) used in previous cluster studies was found to greatly enhance cluster cooling. Laser vaporization is achieved by focusing a 2 mJ, 532 nm pulse from a frequency-doubled Nd:YAG laser (20 Hz repetition rate) onto a rotating, translating silicon rod. The negative ions that pass through a 2 mm diameter skimmer are collinearly accelerated to 1 keV. Mass selection is achieved by a 1 m long beam-modulated time-of-flight mass spectrometer. The mass separated ions then enter the detector region where they are photodetached by a (pulsed) excimer-pumped dye laser. The dyes used for photodetachment of \( \text{Si}^-_4 \) were Coumarin 503 (479–553 nm), Exalite 416 (402–427 nm), DPS (399–415 nm), BBQ (367–405 nm), QUI (368–402 nm), DMQ (346–377 nm), pTp (332–350), and, doubled with a 1/3-barium borate (BBO) crystal, Rhodamine 640 (310–332 nm), and Rhodamine 590 (287–300 nm).
Threshold photodetachment spectra are obtained by adapting the ZEKE spectroscopy method developed by Müller-Dethlefs et al. to negative ion photodetachment. In this experiment, the Si$^-$ is photodetached in the region marked by the $\times$ on Fig. 2. The photoelectrons are extracted with a delayed, pulsed field. This allows the higher energy photoelectrons to spatially separate from the threshold electrons, which have nearly zero kinetic energy. The energetic electrons that scatter away from the ion beam axis are discriminated against by apertures located in the detector region. Those that scatter along the ion beam arrive at the detector at different times from the threshold electrons and are discriminated against by gated integration of the threshold electrons. This combination of spatial and temporal discrimination yields an electron energy resolution of 3 cm$^{-1}$.

As an alternative mode of operation, the photoelectrons can be extracted immediately upon photodetachment. This results in spectral features that are 150 cm$^{-1}$ wide but have considerably higher intensity. While no high resolution information can be obtained in this mode of operation, it is useful as a first order method of locating the threshold electrons, which have nearly zero kinetic energy. This results in spectral features that are 150 cm$^{-1}$ wide but have considerably higher intensity. While no high resolution information can be obtained in this mode of operation, it is useful as a first order method of locating the threshold electrons, which have nearly zero kinetic energy. This combination of spatial and temporal discrimination yields an electron energy resolution of 3 cm$^{-1}$.

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III. RESULTS

The spectrum of Si$^-$ obtained on the threshold photodetachment apparatus is shown superimposed on the photoelectron spectrum of Si$^-$ in Fig. 3. In the ZEKE mode of operation, we saw the two bands labeled $A'$ and $B'$. Band $A'$ corresponds well with band $A$ seen in the PES, but band $B'$ falls primarily on the rising edge of band $B$ in the PES. No structure is seen in the ZEKE spectrum for the remainder of the energy range spanned by the PES band $B$. Band $C'$, which corresponds to band $C$ in the PES, could only be observed in the partially discriminated mode of operation due to its low signal intensity; this is why the features in this band are broader. No signal corresponding to band $X$ (the transition to the Si$^-$ ground state) in the PES could be observed in either the ZEKE or partially discriminated mode. Hence, the three observed bands all involve transitions to excited states of Si$^-$. The bands will now be examined in greater detail.

A. Band $A'$

Band $A'$ in the threshold photodetachment spectrum shows a progression of up to 14 peaks which corresponds to the partially resolved vibrational structure seen previously in the Si$^-$ PES. The PES had to be shifted along the abscissa by $-0.03$ eV in order to fully align the PES and ZEKE progressions. Assuming this shift applies to the entire photoelectron spectrum, the electron affinity of Si$^-$ previously obtained from the PES should be changed slightly to $2.17 \pm 0.01$ eV. Figure 4 shows a finer step, signal averaged scan of this band. Clearly, each member of this progression consists of groups of smaller peaks found to either side of a single, more intense peak. The intense peak in each group is labeled by number and the positions and spacings of these peaks are listed in Table I. The average peak spacing is $312$ cm$^{-1}$.

Figure 5 shows a more expanded scale scan of the two groups of peaks around peaks 3 and 4. The more intense side peaks, labeled $a_n$ through $e_n$, shade to higher photon energy relative to the most intense peak (peak n) in each group, while the less intense side peaks, labeled $f_n$ and $g_n$, shade to lower photon energy. The positions and energies of these side progressions are listed in Table II for the two groups shown in Fig. 4. All of the main and side peaks are between 16 and 20 cm$^{-1}$ wide (FWHM). We note that this pattern of peaks occurs, with some intensity variation, for every group of peaks in band $A'$.

The intensities of peaks $a_n$ through $g_n$ are dependent on source conditions. When we produced ions using a solenoid-type pulsed molecular beam valve (i.e., higher temperature) instead of the piezoelectric valve, $a_n$ and $b_n$ were as intense as the main peak $n$ while $c_n$ through $e_n$ remained unresolved in a broad signal with half the intensity of the $n-a_n-b_n$ triplet. The intensities of peaks $g_n$ and $f_n$ are also dependent on source conditions, although they never exceeded one half the $n$ peak intensity. This source condition dependence indicates that these peaks are due to transitions from vibrationally excited levels of the anion.
or, “hot-band” transitions. The assignments of these peaks are addressed in the following section.

At first glance, peaks \( a_n \) through \( e_n \) appear to belong to one progression with a spacing of \( \sim 25 \text{ cm}^{-1} \). However, the intensity distribution of these peaks indicate otherwise. Peak \( b_n \) is typically of comparable intensity to \( a_n \), whereas peak \( c_n \) is quite small compared to \( b_n \), if it can be resolved at all. Therefore, peaks \( a_n \) through \( e_n \) appear to involve two vibrational modes. For instance, \( b_n \) has an average spacing from \( n = 53 \text{ cm}^{-1} \), and \( d_n \) is \( 51 \text{ cm}^{-1} \) from \( b_n \) on average, and for several of the main spectral features, an \( e_n \) peak can also be seen approximately \( 50 \text{ cm}^{-1} \) to the blue of peak \( d_n \).

The \( a_n \) peaks are spaced approximately \( 30 \text{ cm}^{-1} \) from peak \( n \) for low \( n \), but this spacing decreases down to \( 26 \text{ cm}^{-1} \) to higher values of \( n \). The same effect is seen for the energy difference between \( c_n \) and \( b_n \) in those cases where \( c_n \) is well enough resolved. Therefore, we believe that \( n, b_n, d_n, \) and \( e_n \) belong to a \( 50 \text{ cm}^{-1} \) progression in one mode, and that \( n, a_n, b_n, c_n \) represent shorter \( 30 \text{ cm}^{-1} \) progressions in a second mode.

The side peaks found to the red of the main peak are fewer and less intense. The \( f_n \) peaks are found approximately \( 25 \pm 5 \text{ cm}^{-1} \) to the red of peak \( n \). In some cases, such as for \( n = 5, f_n \) appears to be hardly resolved from the main peak. The \( g_n \) peaks are found approximately \( 53 \pm 5 \text{ cm}^{-1} \) to the red of the main peaks \( n \). Figure 4 shows that the intensities of the \( g_n \) peaks relative to the main peaks is not constant throughout the progression; for \( n = 0 \sim 3 \), the \( g_n \) peaks are fairly prominent, but peaks \( g_4 \) and \( g_5 \) cannot be discerned from the noise. For \( n > 8 \), the \( g_n \) peaks again become apparent.

### B. Band \( B' \)

As can be seen from the ZEKE portion of the spectrum shown in Fig. 3, band \( B' \) is much less intense than band \( A' \). In addition, the progression is much shorter. Note that while band \( A' \) closely matches band \( A \) in the photoelectron spectrum, band \( B' \) covers a much smaller energy range than band \( B \) in the PES. No structure was seen between band \( B' \) and \( 300 \text{ nm} \), even using the partially discriminated cross section mode of the apparatus. Figure 6 shows band \( B' \) on an expanded scale. Because the signal was so much less for this band, the signal-to-noise ratio is not as good as for band \( A' \).

Again, the members of the progression in this band appear as groups of peaks, but the profiles and relative intensities of groups exhibit irregularity. The first three members of the progression are qualitatively similar in profile to those found in the band \( A' \) in that the groups are
dominated by a central intense peak, labeled $n'$, as well as fairly intense side peaks, $a_{v'2}$ and $a_{v'3}$, found to higher photon energy and a less intense side peak, $g_{v'}$, at lower photon energy. The central peaks $n'$ in the first three groups seem to form a short, 300±6 cm$^{-1}$ progression. However, the profiles of the fourth and fifth groups are quite different. There is no peak at the correct position in the fourth group to be a part of the 300 cm$^{-1}$ progression, although the average position of the two intense peaks labeled $d_{v'}$ and $f_{v'}$ is just where peak $3'$ would be expected. In the fifth group, peak $4'$, while apparently part of the main 300 cm$^{-1}$ progression, is noticeably less intense than the peaks to either side. Peak $5'$ can barely be discerned from the noise. Peak positions and spacings for band $B'$ can be found in Table III.

### Table III. Positions and relative spacings of the peaks found in the $B'$ band of Si$_4^-$

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (nm)</th>
<th>Relative spacing (cm$^{-1}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0'$</td>
<td>349.90(12)</td>
<td>0</td>
</tr>
<tr>
<td>$a_{v'}$</td>
<td>349.70(12)</td>
<td>16</td>
</tr>
<tr>
<td>$b_{v'}$</td>
<td>349.35(12)</td>
<td>45</td>
</tr>
<tr>
<td>$g_{v'}$</td>
<td>347.0(12)</td>
<td>239</td>
</tr>
<tr>
<td>$1'$</td>
<td>346.20(12)</td>
<td>305</td>
</tr>
<tr>
<td>$a_{v'}$</td>
<td>345.86(12)</td>
<td>334</td>
</tr>
<tr>
<td>$b_{v'}$</td>
<td>345.40(14)</td>
<td>372</td>
</tr>
<tr>
<td>$g_{v'}$</td>
<td>343.61(12)</td>
<td>529</td>
</tr>
<tr>
<td>$2'$</td>
<td>342.69(12)</td>
<td>602</td>
</tr>
<tr>
<td>$a_{v'}$</td>
<td>342.41(12)</td>
<td>625</td>
</tr>
<tr>
<td>$b_{v'}$</td>
<td>342.13(14)</td>
<td>649</td>
</tr>
<tr>
<td>$g_{v'}$</td>
<td>340.22(12)</td>
<td>814</td>
</tr>
<tr>
<td>$f_{v'}$</td>
<td>339.45(8)</td>
<td>880</td>
</tr>
<tr>
<td>$a_{v'}$</td>
<td>339.00(8)</td>
<td>918</td>
</tr>
<tr>
<td>$b_{v'}$</td>
<td>338.60(11)</td>
<td>954</td>
</tr>
<tr>
<td>$g_{v'}$</td>
<td>337.21(17)</td>
<td>1076</td>
</tr>
<tr>
<td>$f_{v'}$</td>
<td>336.26(11)</td>
<td>1160</td>
</tr>
<tr>
<td>$4'$</td>
<td>336.96(11)</td>
<td>1186</td>
</tr>
<tr>
<td>$a_{v'}$</td>
<td>335.61(15)</td>
<td>1217</td>
</tr>
<tr>
<td>$5'$</td>
<td>332.71(11)</td>
<td>1477</td>
</tr>
</tbody>
</table>

*Error for spacing is ±14 cm$^{-1}$.

### C. Band $C'$

We were restricted to examining this band using the partially discriminated cross section mode of the apparatus due to very low photoelectron signal. The low signal is due to small photodetachment cross section threshold for this state and lower photodetachment laser power.

The broad features of band $C'$ shown in Fig. 3 are roughly 200 cm$^{-1}$ wide and are separated by approximately 430 cm$^{-1}$ peak to peak. The broad peaks are not perfectly symmetric; there are probably many sequence bands (as were seen for the higher resolution sections of the spectrum) and/or combination features contributing to the profile of these features.

### IV. Analysis and Discussion

According to Rohlfing and Raghavachari, the $^2B_{2g}$ anion ground state has the valence orbital configuration $\cdots(b_{3u})^2(b_{3u})^2(a_g)^2(b_2)^2(b_{2g})^1$. Electrons removed from either the $b_{1u}$ or the $b_{2g}$ orbitals can depart via s-wave photodetachment, while this is not the case for the $b_{2g}$ or $a_g$ orbitals. Therefore, assigning the $C$ PES in Ref. 4, (see band labels on Fig. 1) we expect to see bands $A$ and $C$ in the ZEKE spectrum, which we do, since these states result from the removal of an electron from the $b_{1u}$ and $b_{2g}$ orbitals, respectively. Band $X$ in the PES is not seen in the ZEKE spectrum, which is consistent with its assignment to the $^4A_g + e^- \rightarrow ^2B_{2g}$ transition. This transition involves removing the $b_{2g}$ electron, which would depart as a p wave. Band $B$ seen in the PES was assigned to the $^2B_{2g} + e^- \rightarrow ^2B_{2g}$ transition, corresponding to removal of an $a_g$ electron. This transition, therefore, should not be apparent in the ZEKE spectrum, but we do observe band $B'$ which corresponds to the rising edge of band $B$ in the PES. As discussed below, we believe band $B$ is due to overlapping electronic transitions, one of which can occur by s-wave detachment. We now consider all three bands in the ZEKE spectrum in more detail.

#### A. Band $A'$

The energy of band $A'$ and the fact that we observe it in the ZEKE spectrum is consistent with the ab initio assignment of this band to the $^3B_{3u} + e^- \rightarrow ^2B_{2g}$ transition. The progression of the central peaks (peaks $n$ in Fig. 4) can be fit with the harmonic frequency $\omega_n = 312 \pm 1$ cm$^{-1}$ and a very small anharmonic constant $\omega_n \chi_n = 0.3 \pm 0.1$ cm$^{-1}$. The harmonic frequency is very close to the ab initio value of 306 cm$^{-1}$ for the $\nu_3(a_g)$ mode in the $^3B_{3u}$ state. Moreover, the ab initio geometries for Si$_4^-$ and the $^3B_{3u}$ state of Si$_4^-$, which are shown in Fig. 7 along with the $v_2$ and $v_1$ (a$_g$) normal modes of the $^3B_{3u}$ neutral (the force constants for determining the normal modes were obtained from our own ab initio calculations on Si$_4^-$) suggest a large displacement along the $v_2$ normal coordinate upon photodetachment, but almost no displacement along the higher frequency $v_1$ normal coordinate. Hence, the $v_2$ mode should be the only active vibration in the ZEKE spectrum.

We therefore assign peaks $n$ to the $20$ progression.
TABLE IV. Excitation energies for several of the low-lying states of $\text{Si}_4$.

<table>
<thead>
<tr>
<th>State of $\text{Si}_4$</th>
<th>$T_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3B_{1u}$</td>
<td>2.01 ± 0.02</td>
</tr>
<tr>
<td>$^3B_{3u}$</td>
<td>1.37 ± 0.01</td>
</tr>
<tr>
<td>$^3B_{3u}$</td>
<td>0.815 ± 0.010</td>
</tr>
<tr>
<td>$^1A_g$</td>
<td>0</td>
</tr>
</tbody>
</table>

(E.A. = 2.17 ± 0.01)

Although the assignment of the $2^u$ progression is straightforward, locating the origin is somewhat more ambiguous. Peak 0, located at 415.27 nm, appears to be the lowest energy peak in the 32 cm$^{-1}$ progression, but one could argue that there is a small peak buried under noise at 312 cm$^{-1}$ lower in energy (420.68 nm), or even 624 cm$^{-1}$ to the red of peak 0 (426.28 nm) where no detectable electron signal was seen.

We attempted to determine the location of the origin and the actual normal mode displacement by performing a single mode ($v_2$) Franck–Condon simulation of the spectrum. Simulations performed assuming the origin was at 415.27 nm [with $\Delta Q$ of 0.219 ± 0.008 Å (amu)$^{1/2}$], 420.68 nm [420.68 nm $\Delta Q$ = 0.235 ± 0.008 Å (amu)$^{1/2}$], or 426.28 nm [426.28 nm $\Delta Q$ = 0.259 ± 0.008 Å (amu)$^{1/2}$] all satisfactorily matched the experimental progression. However, based on the $ab$ initio geometries and force constants, we can calculate the $v_2$ normal mode displacement between the anion and neutral. We find this to be 0.208 Å (amu)$^{1/2}$, which is in best agreement with the normal coordinate displacement assumed for the simulation with the origin at 415.27 nm. We therefore take this to be the origin. The excitation energy of the $^3B_{3u}$ state is then 0.815 ± 0.010 eV (listed in Table IV) which is in good agreement with the 0.85 eV excitation energy calculated by Rohlfing and Raghavachari.$^4$

We next consider the set of peaks $g_n$, each of which is located 53 cm$^{-1}$ to the red of the corresponding central peak $n$. The bimodal intensity distribution of these peaks, passing through a minimum at $n = 5$–6, can be explained by assigning them to a hot-band progression in the $v_2$ mode originating from the $v_2 = 1$ level of the anion, i.e., a $2^u$ progression. The intensity minimum can be qualitatively understood by referring to Fig. 8, which shows anion and neutral harmonic potential energy curves displaced along the $Q_2$ coordinate by 0.219 Å (amu)$^{1/2}$, the displacement that best reproduced the intensity distribution of the main progression (peaks $n$). This displacement is such that a node in the neutral $v_2 = 6$ wave function coincides with one of the the maxima of the anion $v_2 = 1$ wave function, causing the overlap to be close to zero. Based on this assignment, the $v_2$ frequency in the anion is 365 cm$^{-1}$, quite close to the $ab$ initio frequency$^4$ of 383 cm$^{-1}$. The intensity distribution of peaks $n$ and $g_n$ can be satisfactorily reproduced in a one-dimensional simulation (not shown) where the vibrational temperature of the anions is assumed to be 200 K.

The large geometry change and fairly large frequency change in the $v_2$ mode between the anion and neutral can be explained by considering the orbital from which the electron is removed in the neutral–anion transition. The $b_{1u}$ orbital is formed by the (in-plane) $p_\sigma$ orbitals (see Fig. 7) which effectively bonds the silicon atoms labeled 1 and 3. Removal of an electron from this orbital will weaken this bond, resulting in the longer bond distance and lower $v_2$ frequency in the neutral, since this mode primarily involves the stretching of $r_6$. 

![FIG. 7. Calculated geometries of the ground $^2B_2$ anion state and the neutral $^3B_{3u}$ state (Ref. 4), the orbital from which an electron is removed in the transition between the two states, and the normal coordinates of the $^3B_{3u}$ state of $\text{Si}_4$.](image)

![FIG. 8. One-dimensional potential energy curves for the anion and neutral $v_2$ modes. The anion potential is displaced by the amount determined in the simulation of band $A'$.](image)
We next consider the other vibrational features in band $A'$, peaks $a_n-f_n$. As mentioned earlier, these peaks originate from vibrationally excited levels in the anion, and we assign them to sequence bands in modes other than the $v_2$ mode, that is, $2\sigma_m^1$, $2\sigma_m^2$, etc., transitions. There are five other normal modes of Si$_4$/Si$_4^-$ that could be contributing to this structure. However, using a vibrational temperature of 200 K as a guideline, significant population is expected only in the four lowest frequency modes of the anion. In order of increasing frequency, these are calculated to be the $v_6$ (165 cm$^{-1}$), $v_5$ (295 cm$^{-1}$), $v_2$ (383 cm$^{-1}$), and $v_1$ (390 cm$^{-1}$) modes. The normal modes are shown in Fig. 7.

The $v_2$ mode has already been accounted for. The $f_n$ peaks, each of which lies 25 cm$^{-1}$ to the blue of the main peak $n$, are of comparable intensity to the most intense $g_n$ peaks, and likely originate from the $v=1$ level of a mode close in frequency to the $v_2$ mode. According to the $ab$ initio results, the most likely candidate is the $v_3$ mode, and we therefore assign peaks $f_n$ to the $2\sigma_5^1$ progression. Although we cannot directly extract the $v_3$ anion and neutral frequencies from the peak positions, they do yield the difference between the anion and neutral frequencies, and show that the $v_3$ mode is 25 cm$^{-1}$ lower in the neutral. This is consistent with the $ab$ initio results, which give $v_3$ = 367 cm$^{-1}$ in the neutral, 23 cm$^{-1}$ less than the calculated anion frequency. As discussed earlier, peaks $a_n-e_n$ to the red of peak $n$ appear to be sequence bands composed of two overlapping progressions. The presence of sequence bands to the red of the central peak means that the vibrational modes involved have higher frequencies in the neutral than in the anion. This is in contrast with the $ab$ initio results, for which all of the frequencies for the Si$_4^-$ $3\Sigma_u^-$ state are lower than in the anion. Since the leading members of these progressions, peaks $a_n$ and $b_n$, are quite intense, these progressions most likely involve the two lowest frequencies of the anion, the $v_3$ and $v_6$ modes. From the positions of peaks $a_n$ and $b_n$, relative to peak $n$, the frequencies of one of these modes is 27 cm$^{-1}$ higher in the neutral than in the anion, while the other is 52 cm$^{-1}$ higher in the neutral. In contrast, the $ab$ initio calculations predict the $v_3$ and $v_6$ frequencies to be higher in the anion by 118 and 8 cm$^{-1}$, respectively.

We therefore have two possible assignments for these peaks. In one assignment, peak $a_n$ is the $2\sigma_5^1$ transition and peak $b_n$ is primarily the $2\sigma_5^2$ transition (with some contribution from the $2\sigma_6^2$ transition). These assignments and those of peaks $c_n-e_n$ are listed in Table II. In the other assignment, $v_4$ and $v_6$ are switched. In order to better choose between these assignments, we can simulate the spectrum using the four modes considered above ($v_2$, $v_3$, $v_5$, $v_6$). We do this first for the assignment in Table II. For the $v_3$ and $v_6$ modes, we need to assume values for the neutral frequencies, and these will fix the anion frequencies. If we choose the $ab$ initio values for the neutral frequencies, the anion frequencies are those given in Table V. If we choose the frequencies from the peak positions, they do yield the values for the neutral frequencies that are close in frequency to the calculated frequencies, but are still quite a bit lower.

Another option is to use the $ab$ initio $v_3$ and $v_6$ frequencies for the anion (see Table V), and fix the neutral frequencies (listed in Table V). The temperatures were fit paying closest attention to peak groups with $n=3$ and 4, since our data is best for these (see inset, Fig. 9). The reasonable fit between the simulated and experimental spectrum using vibrational temperatures close to 200 K for all four modes offers indirect support both for the assignment of peaks $a_n-e_n$ and for using the $ab$ initio frequencies for the neutral. While different modes have different cooling efficiencies in a free jet expansion, we would expect the temperatures of the remaining modes to be in the neighborhood of 200 K, the appropriate temperature for the $v_3$ mode, particularly if they have similar or lower frequencies. If we use the alternate assignment proposed above, with the $v_3$ and $v_6$ modes switched from Table II, and use the $ab$ initio values for the neutral frequencies, then the anion frequencies are $v_3$ = 150 cm$^{-1}$ and $v_6$ = 107 cm$^{-1}$, and the required vibrational temperatures are 380 and 107 K, respectively (these values are included parenthetically in Table V). This is a noticeably larger deviation from 200 K than the values obtained using the former assignment, and makes this assignment somewhat less desirable.

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frequencies accordingly. Using the peak assignments in Table II, we require vibrational temperatures of 650 and 450 K for the $v_4$ and $v_5$ modes, respectively. These temperatures for the lowest frequency modes seem unreasonably large compared to the 200 K temperature for the $v_2$ mode. A similarly large deviation is obtained using the alternate assignment assuming the ab initio anion frequencies.

Overall, the peak assignments in Table II and the frequencies listed in Table V seem the most reasonable of all.

The spectra support the ab initio geometries for Si$_4^-$ and the Si$_4^+$ excited state, as well as the ab initio frequencies for the anion and neutral $v_1$ and $v_2$ modes. However, the spectra are inconsistent with the ab initio $v_2$ and $v_6$ frequencies. The $v_2$ frequency for the anion is particularly suspect, since it lies well above the predicted neutral frequency, whereas our spectrum shows it should be less than the neutral frequency. Moreover, a high vibrational temperature for the $v_1$ mode is always needed to simulate the spectrum if the ab initio value is used. It is possible that the large discrepancy between the ab initio Si$_4$/Si$_4^-$ $v_3$ frequency difference and the observed frequency difference is due to an incorrect assignment of the $b_5$ peaks. For instance, $b_{-6}$ could be due to a combination band; if $b_{-6}$ were due to the $2^3 e^{-2} + 2^3 g^{-1}$ transition, its position would be in fairly good agreement with the calculated $v_3$ frequency. However, were this the case, peak $b_0$ (found 50 cm$^{-1}$ from the origin) would not appear in the spectrum. Also, the intensity of the $b_{-6}$ peaks is too high for a $\Delta v=2$ transition in a non totally symmetric mode. Thus we believe our assignment of the $b_{-6}$ peaks to sequence band transitions is correct. In any case, independent measurements of either the anion or neutral $v_2$ and $v_6$ frequencies would result in a more complete understanding of the ZEKE spectrum.

B. Band $B'$

Rohlfing and Raghavachari assigned band $B$ shown on the PES (Fig. 1) to the $3^1 B_g + e^- \rightarrow 2^1 B_g$ transition, where the $3^1 B_g$ state has a $C_{2v}$ structure resulting from a slight distortion of the $3^1 B_{2g}$ ($D_{2h}$) state. They pointed out that the irregular spacings of the band may be due to contributions from the nearby $3^1 B_{1g} - 1^1 B_{2g}$ and $1^1 B_{1u}$ states. However, only the $1^1 B_{1u}$ state is accessible from the anion by s-wave detachment. This suggests that band $B'$ in the ZEKE spectrum and the leading edge of band $B$ in the photoelectron spectrum are due to the $1^1 B_{1u} + e^- \rightarrow 2^1 B_{2g}$ transition. The $1^1 B_{1u}$ state is the singlet counterpart of the $3^1 B_{1u}$ state responsible for band $A'$, so the apparent origin of band $B'$ at 349.90 nm implies a singlet–triplet splitting of 0.558 eV for the $B_{1u}$ state. This is lower than the calculated splitting, 1.04 eV, but the disagreement is not so unreasonable considering the degree of difficulty in accurately calculating singlet–triplet splittings in complex molecules.

The profile of band $B'$ is very different from band $A'$, with the intensity of band $B'$ falling off after only a few peaks. Moreover, the vibrational structure in band $B'$ is irregular. As mentioned in Sec. III, the first three groups of peaks in this band (Fig. 5) are similar to the peak groups in the band $A'$. The spacing of the central peaks 0'–2' is 300(8) cm$^{-1}$, and the fairly intense sequence bands occurring to the red of these features ($g_{1/2}$) are spaced such that the anion frequency is approximately 365 ± 5 cm$^{-1}$. Thus the $n'$ peaks appear to be a progression in the $v_2$ mode of the neutral $1^1 B_{1u}$ state, with a frequency 12 cm$^{-1}$ lower than the $v_2$ mode in the $3^1 B_{2u}$ state. The fourth group of peaks is very different; it is an intense doublet separated by approximately 38 cm$^{-1}$. These peaks, $f_{1/2}$ and $a_{1/2}$, are separated by 279 and 317 cm$^{-1}$ from the peak 2', so it seems that the 300 cm$^{-1}$ progression stops at peak 2'. It is true that the signal-to-noise ratio of this band is not very good and the progressions of the $v_1$ and $v_2$ peaks are almost within the experimental uncertainty of the 300 cm$^{-1}$ progression. However, the $a_{1/2}$ and $f_{1/2}$ peaks are well resolved from each other, while the peaks 2', 1', and 0' are poorly resolved from the adjacent transitions. Thus the pattern of transitions in the fourth group is clearly different from the lower energy groups of peaks.

Since the band $B'$ does not span the energetic extent of band $B$ in the PES, there must be at least one dark state lying close to the $1^1 B_{1u}$ state. By this, we mean a Si$_4$ electronic state which is not accessible by s-wave detachment and therefore is seen in the PES but not the ZEKE spectrum; this includes all three of the other electronic states predicted to occur in the vicinity of band $B$. Hence, a possible explanation for the vibrational irregularity of band $B'$ is that the higher vibrational levels of the $1^1 B_{1u}$ state are vibronically coupled to one of these dark states.

As examples of possible vibronic coupling schemes; any totally symmetric vibrational level of the $1^1 B_{1u}$ state could be coupled with odd vibrational levels in a $b_{1u}$ mode of the $1^1 B_{2g}$ state, odd $b_{1g}$ levels of the $3^1 B_{1u}$ state, or odd $b_{u}$ levels of the $3^1 B_{2g}$ state. Given that the three candidate states for vibronic coupling are all predicted to lie within 0.3 eV of where we observe the $1^1 B_{1u}$ state, one might expect the dominant coupling to be with the $1^1 B_{2g}$ state, as this is the only nearby state with the same spin multiplicity.

The peak pattern for the fourth group is what one might expect under the following circumstances. Suppose a $\nu_4=1$ odd level ($b_{1u}$ vibrationally symmetric—see Fig. 7) of the $1^1 B_{2g}$ state were accidentally degenerate with the $\nu_3=3$ level of the $1^1 B_{1u}$ state, at the energy where peak 3' would normally occur. The two vibronically coupled levels would mix and repel one another, and a 38 cm$^{-1}$ splitting via this interaction would yield peaks $a_{1/2}$ and $f_{1/2}$. Peak $a_{1/2}$ then consists of two overlapped transitions—one due to the higher energy transition resulting from the vibronic coupling interaction, and the other from the transition analogous to peaks $a_{1/2}$ and $f_{1/2}$ (see below). Clearly, such a mechanism must be regarded as speculative, but it is certainly not unreasonable given the large number of nearby electronic states.

The $4'$ group is most likely affected in a similar man-

ner, but due to the poor S/N, it is difficult to get a precise idea of what could be happening with it. The chance of vibronic coupling only increases at higher energies due to presence of more combination bands with the appropriate vibronic character, so we would only expect it to be increasingly difficult to analyze these higher energy peaks.

There have been several other issues regarding this band. It has been mentioned that the profiles of the first three groups of peaks in the \( B' \) band are qualitatively similar to those in the \( A' \) band, but not exactly. For example, the spacing between peaks \( a_n'a_n' \) and \( n' \) in band \( B' \) is slightly smaller than between peaks \( a_n' \) and \( n \) in band \( A' \). If the \( a_n' \) peaks are due to sequence bands in the \( \nu_3 \) mode, a difference between the neutral singlet and triplet \( \nu_3 \) frequencies of about 5 to 10 cm\(^{-1} \) (the triplet frequency being higher) would account for this. Also, the origin of this band has not been definitively identified, although we assign it to peak \( 0' \), the central peak of the lowest energy group identified with band \( B' \). However, the lower signal to noise associated with band \( B' \) may cause the actual origin to be obscured. The excitation energy of the \( 1B_{3u} \) state assuming peak \( 0' \) to be the origin is 1.37±0.010 eV (see Table IV).

While we cannot determine the origins of the \( 1B_{3g}, 3B_{1g}, \) or \( 3B_{1u} \) states, our vibronic coupling hypothesis requires at least one of them to lie quite close to the \( 1B_{3u} \) state.

### C. Band \( C' \)

While not much information can be extracted from the broad features comprising band \( C' \), a few words on its assignment are warranted. This band, which was assigned to the \( 3B_{1u}+e^- \rightarrow 2B_{2g} \) transition,\(^4\) lies approximately 1.2 eV above band \( A' \). This raises the possibility that band \( C' \) is due to the transition to the \( 1B_{3u} \) state (the singlet–triplet splitting for \( B_{3g} \) was calculated to be 1.04 eV) and that band \( B' \) is the \( 3B_{1u}+e^- \rightarrow 2B_{2g} \) transition. However, this possibility is unlikely for the following reason. From the \( ab \) initio geometries, the \( \nu_1 \) mode should be active in transitions to the \( 3B_{1u} \) state. The \( \nu_1 \) frequencies of all of the excited \( D_{3h} \) states are around 400 cm\(^{-1} \) or greater. The \( B' \) progression is approximately 300 cm\(^{-1} \), while the peak spacing in band \( C' \) is roughly 430 cm\(^{-1} \), consistent with a \( \nu_1 \) progression. We therefore believe that the assignment of band \( C' \) made by Rohlfing and Raghavachari is correct.\(^4\)

### V. CONCLUSION

The results presented here represent a far more detailed experimental probe of the vibrational and electronic structure of silicon tetramer than our previous photoelectron spectroscopy study. We have obtained several vibrational frequencies for the anion and various electronic states of the neutral, particularly the \( 1B_{3u} \) excited state, as well as excitation energies for several electronic states.

Our results also emphasize the interaction between theory and experiment in understanding the spectroscopy of clusters. The role of \( ab \) initio calculations in interpreting these spectra cannot be overemphasized. In the absence of experimental force constants for Si\(_4\), \( ab \) initio calculations are needed to perform any reasonable assignment of the observed vibrational progressions. Moreover, given the complex electronic structure of a species such as Si\(_4\), the assignment of electronic bands to specific neutral–anion transitions also requires some \( ab \) initio input.

Our experimental results provide a detailed comparison with the predictions. We find from band \( A' \) that the excitation energy for the \( 1B_{3u} \) state is in excellent agreement, as are the vibrational frequencies for the \( \nu_3 \) mode in the anion and this state of the neutral. The sequence band structure in band \( A' \) is consistent with the \( ab \) initio values for the \( \nu_3 \) mode in the anion and neutral, but not with the \( ab \) initio values for the \( \nu_4 \) and \( \nu_5 \) modes. Our results also show that band \( B \) in the Si\(_4^-\) photoelectron spectrum is due to transitions to overlapping electronic states, as suggested in the calculations, but the ZEKE spectrum implies that the lowest energy of these is the \( 1B_{3u} \) state, whereas the calculations predict this to be about 0.5 eV higher than where we observe it. Finally, on the basis of the observed vibrational progression, we find the \( ab \) initio assignment of band \( C \) to the transition to the \( 1B_{3u} \) state to be reasonable.

We feel that these comparisons between experiment and theory will become even more essential as we begin to study the larger Si clusters via threshold photodetachment spectroscopy. Many of these are predicted to exhibit several low-lying structures with very different geometries. A comparison of experimental and theoretical vibrational frequencies and electronic excitation energies will facilitate sorting out these possible cluster structures.

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C. C. Arnold and D. M. Neumark: Study of Si$_4$ and Si$_8$.