Photoelectron spectroscopy and zero electron kinetic energy spectroscopy of germanium cluster anions

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Anion photoelectron spectra of Ge_n^-, $n=2-15$, have been measured using an incident photon energy of 4.66 eV. In addition, the spectra of Ge_2^-, Ge_3^-, and Ge_4^- have been measured at photon energies of 3.49 and 2.98 eV. From these spectra the electron affinity of the corresponding neutral cluster has been determined. Vibrational frequencies and term values for several electronic states of Ge_2^- and Ge_3^- have been determined. Vibrational structure in the $^3B_{3u}$ excited state of Ge_4 has been resolved using zero electron kinetic energy (ZEKE) photoelectron spectroscopy. The assignment of the spectra of Ge_3^- and Ge_4^- is facilitated by a comparison to the similar spectra of Si_3^- and Si_4^-, respectively. The spectra of the larger clusters, Ge_n^-, $n=5-15$, are characterized by many broad structureless features which indicate the presence of multiple electronic transitions. Several of these were assigned based on comparison with previous *ab initio* calculations on germanium and silicon clusters. © *1996 American Institute of Physics.* [S0021-9606(96)01108-1]

I. INTRODUCTION

The study of semiconductor clusters by photoabsorption and photoionization methods provides a means of determining how the electronic structure of an element changes as one proceeds from a single atom to a bulk solid. Anion photodetachment spectroscopy is particularly well suited for such studies as it affords the preparation of an internally cold beam of mass selected ions, thus avoiding the inherent problem in the study of clusters of separating the cluster of interest from the other species. Recent work from this laboratory includes studies of carbon,[1] silicon,[2–7] and indium phosphide[8] clusters using both anion photoelectron spectroscopy and zero-electron kinetic energy (ZEKE) spectroscopy. In this paper we present photoelectron spectra of Ge_n^- ($n=2-15$) and the ZEKE spectrum of Ge_4^-.

Recent work on small silicon clusters provides an excellent example of how photodetachment, in conjunction with other experiments and *ab initio* calculations, can be used to learn about the vibrational and electronic structure of covalently bound clusters. Kitsopoulos *et al.*[2] obtained vibrationally resolved photoelectron spectra of Si_3^- and Si_4^-, and proposed a tentative assignment based on the calculations on small silicon clusters that were available at the time. Subsequent calculations by Rohlfing and Raghavachari[9] helped elucidate the electronic structures of these two systems, and ZEKE studies by Arnold *et al.*[6,7] on Si_3^- and Si_4^- further clarified the assignments. Honea *et al.*[10] have used a combination of *ab initio* quantum mechanical calculations and Raman spectroscopy to determine vibrational frequencies and symmetries for the ground electronic states of Si_4, Si_6, and Si_7. From these experiments and calculations there is now a good understanding of the spectroscopy of these small silicon systems. Owing to the similarity between the anion photoelectron spectra of small silicon and germanium clusters, as was demonstrated by Cheshnovsky *et al.*,[11] these results for silicon clusters should be useful for the assignment of the photoelectron spectra of small germanium clusters obtained under similar experimental conditions.

Compared to the wealth of spectroscopic data for carbon[12] and silicon clusters, there is very little known about the spectroscopy of germanium clusters. Froben and Schulze[13] measured Raman and fluorescence spectra from Ge molecules deposited onto a cryogenic matrix and assigned various vibrational frequencies to Ge_2, Ge_3, and Ge_4, but the absence of mass separation makes these assignments problematic. The anion photoelectron spectroscopy study on Ge_n^-, $n=3-12$, by Cheshnovsky[11] represents the first spectroscopic work on mass-selected germanium clusters. These spectra were taken using an incident photon energy of 6.42 eV at a resolution of about 150 meV fwhm, yielding electron affinities and the first glimpse of the electronic complexity of these clusters. More recently, two detailed studies of Ge_2 have been reported. Magneto-infrared spectra of Ge_2 have been measured by Li *et al.*[14] in rare gas matrices at 4 K. They determined that the lowest $^3\Pi_u$ state of Ge_2 has a term value of $694\pm2\ \mathrm{cm}^{-1}$, a vibrational frequency of $308\ \mathrm{cm}^{-1}$, and an anharmonicity ($\omega_e\chi_e$) of $0.5\ \mathrm{cm}^{-1}$. Arnold *et al.*[15] have studied Ge_2^- with zero electron kinetic energy (ZEKE) spectroscopy. In addition to determining accurate term values and vibrational frequencies for the low lying electronic states of Ge_2 and Ge_2^-, the high spectroscopic resolution afforded by this technique ($3\ \mathrm{cm}^{-1}$) permitted accurate determination of the zero field splitting for each component of the $^3\Sigma_g^-$ state and the spin–orbit components of the $^3\Pi_u$ state.

There have been numerous theoretical studies of small germanium clusters aimed at determining electronic properties for Ge_2,[16–27] and the most stable geometric configuration for larger clusters.[28–36] The most stable conformations of the

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neutral clusters Ge_5, Ge_6, and Ge_7 have been determined by Pacchioni and Koutecky[31] using a pseudopotential method followed by configuration interaction. Correlation effects were taken into account using multireference doubly excited configuration interaction (MRDCI). For Ge_5 the most stable conformation is found to have a trigonal bi-pyramidal geometry (D_{3h}) and the ground electronic state is ${}^3A_2'$. The ground state of Ge_6 is found to have C_{2v} symmetry and a ${}^1A_1$ ground state. Pacchioni and Koutecky[31] only considered the D_{5h} bi-pyramidal structure for Ge_7 and determined a ground state of ${}^1A_1'$ symmetry. No *ab initio* quantum mechanical calculations exist for the larger germanium clusters studied in the present work. The only reported geometries for Ge_n, $n=8-14$, reported in the literature were calculated by Antonio *et al.*[30] using molecular dynamics simulations. Saito *et al.*[37] determined the structures of group-IV microclusters ($n=2-20$) using an anisotropic model potential.

In the present work we report anion photoelectron spectra for small germanium clusters (Ge_n^-, $n=2-15$) at a resolution of about 10 meV fwhm which is significantly better than that in the work of Cheshnovsky *et al.*[11] We also report higher resolution ZEKE spectrum of Ge_4^-. From the photoelectron spectra we obtain vibrational frequencies for several electronic states of Ge_2 and Ge_3, and the ZEKE spectrum yields vibrational structure for an excited electronic state of Ge_4. The photodetachment spectra of Ge_3^- and Ge_4^- can be interpreted based on the recent calculations on small germanium clusters,[16,25,30–36] and from a comparison with results for corresponding small silicon clusters—results which were not available in 1987 when the previous study was undertaken. Although our spectra of the clusters with $n \geqslant 5$ do not show any resolved vibrational structure, some of the electronic features are better resolved than in Ref. 11.

II. EXPERIMENT

The anion photoelectron spectrometer used in the present study has been described in detail previously,[38] therefore only a brief description will be given here. A plasma is produced by focusing the output of a Nd:YAG laser (532 nm, second harmonic) on a translating and rotating rod[39] of germanium (ESPI, stated purity of 99.9999%). The resulting plasma is entrained in a supersonic expansion of a noble gas from a pulsed nozzle. Using this source, germanium clusters up to Ge_{35}^- were produced in detectable quantities. However, there were not enough of these larger clusters to permit measurement of a reasonable photoelectron spectrum. The negative ions that are formed are cooled internally during the expansion. The ions are then pulsed out of the ion source and into a Wiley–McLaren-type[40] time-of-flight mass spectrometer. The ions are accelerated to the same potential and separate out in time owing to their different mass to charge ratios. The resolution of the ion time-of-flight channel ($m/\Delta m$) was about 250 and was sufficient to resolve all the isotopic peaks for each germanium cluster up to and including Ge_4^-.

A pulse from a second Nd:YAG laser is timed so as to photodetach the ion packet of interest. The spectra of Ge_2^-, Ge_3^-, and Ge_4^- were measured at mass to charge ratios of 146, 218, and 290, respectively. For the larger clusters (Ge_5^- to Ge_{15}^-) the laser was timed so as to intersect the ion beam at the maximum of the corresponding peak in the mass spectrum. The third (355 nm, 3.49 eV) and fourth (266 nm, 4.66 eV) harmonics of the Nd:YAG laser were used in the present study. In addition, 416 nm (2.98 eV) laser light was produced by Raman shifting the third harmonic by passage through a high pressure (about 300 psi, path length of about 20 cm) cell containing hydrogen. The energies of the resulting photoelectrons were determined by time-of-flight down a field-free, calibrated flight tube. The resolution of the electron channel has been determined to be 8 meV fwhm at an electron kinetic energy (eKE) of 0.65 eV and degrades as $(\mathrm{eKE})^{3/2}$. Most spectra are reported at a laser polarization angle $\theta=55°$ with respect to the direction of electron detection; this is the "magic angle" at which the anisotropic angular distributions do not affect relative intensities of electronic bands. In some cases, the overall signal-to-noise was better at $\theta=90°$, and some spectra are reported at that polarization angle.

The threshold photodetachment spectrometer used in the present work to measure the ZEKE photoelectron spectrum of Ge_4^- has been described in detail previously.[41,42] Briefly, the cluster ions were produced using the same laser vaporization source described earlier. The negative ions that were produced were accelerated to 1 keV and were separated by time of flight. The photodetachment pulse from an excimer-pumped tunable dye laser was timed so as to intersect the

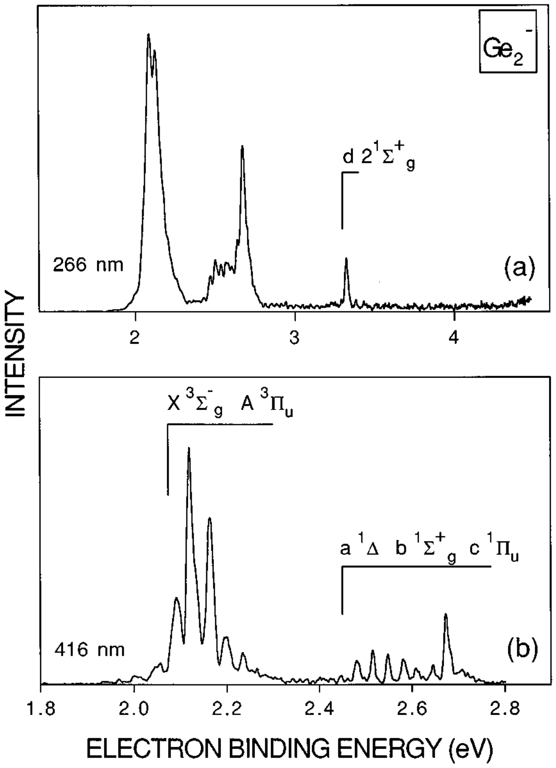

FIG. 1. Anion photoelectron spectra of Ge_2^- measured in the present work at a laser polarization angle of 55°, as a function of laser wavelength. (a) 266 nm and (b) 416 nm.

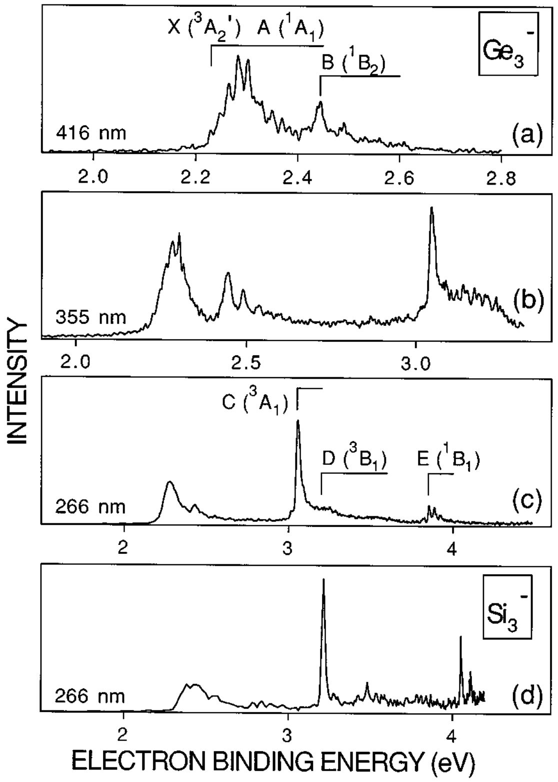

FIG. 2. Anion photoelectron spectra of Ge_3^- measured in the present work as a function of laser wavelength. (a) 416 nm, laser polarization 90°, (b) 355 nm, laser polarization 90°, (c) 266 nm, laser polarization 55°. Panel (d) shows the anion photoelectron spectrum of Si_3^- measured by Kitsopoulos *et al.*[2] at 355 nm and a laser polarization of 55° and reported on a binding energy scale. Assignments are discussed in text.

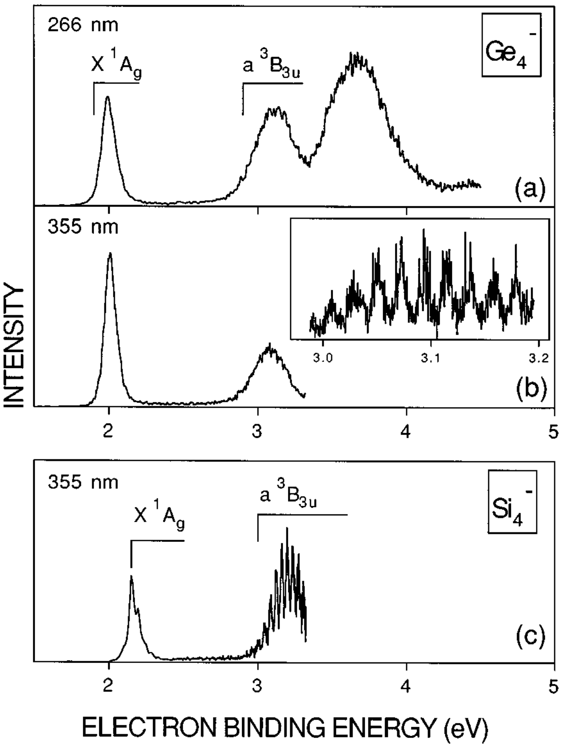

FIG. 3. Anion photoelectron spectra of Ge_4^- measured in the present work as a function of laser wavelength at a laser polarization of 90°. (a) 266 nm and (b) 355 nm. Panel (c) shows the anion photoelectron spectrum of Si_4^- measured by Kitsopoulos *et al.*[2] at 355 nm and a laser polarization of 55° and reported on a binding energy scale. The inset to panel (b) shows the ZEKE photoelectron spectrum of Ge_4^- measured in the present work from 2.99 to 3.20 eV (388 to 415 nm). Assignments are discussed in text.

cluster ion of interest. The spectrometer is designed to efficiently collect those electrons which are produced with nearly zero electron kinetic energy and to strongly discriminate against the other, higher energy, electrons. Using this technique a resolution of 3 cm^{-1} fwhm (0.4 meV fwhm) is achievable. This detection scheme is similar to that designed by Müller-Dethlefs *et al.*[43,44] for ZEKE photoionization experiments on neutral species.

III. RESULTS AND DISCUSSION

A. General

The photoelectron spectra of the germanium clusters studied in the present work are reported as a function of electron binding energy, E, from Figs. 1–6. The binding energy of the electron in the anion is independent of the photon energy, $h\nu$, and is given by

$$E=h\nu-eKE, \tag{1}$$

$$E=EA+T_0^0+E_v^0-T_0^--E_v^- . \tag{2}$$

In these equations, EA is the electron affinity of the neutral cluster, T_0^0 and T_0^- are the term values of the accessed states of the neutral and ion, respectively, and E_v^0 and E_v^- are the vibrational energies (above the zero point energy) of the neutral and the anion, respectively. It should be noted that the states of higher internal energy in the neutral lie at higher electron binding energies. As alluded to in the experimental section, varying the photon energy has two effects on the spectrum. First, the transition probability (cross section) will vary as a function of energy. Second, the electron resolution of the spectrometer varies as a function of the kinetic energy of the electron and increases as the electron kinetic energy decreases.

The electron affinities determined in the present work for the clusters of germanium are given in Table I. The electron affinity of Ge_2^- was measured accurately by Arnold *et al.*[15] The electron affinities of Ge_3^- and Ge_4^- were determined from the estimated positions of the 0–0 transitions in the photoelectron spectrum measured at 416 nm for each molecule. The presence of overlapping electronic states (as is the case for Ge_3^-) and the lack of clearly resolved vibrational structure (as is the case for Ge_4^-) increase the experimental uncertainty of the electron affinities for these systems. Owing to the lack of resolved vibrational structure in the ground electronic states of the larger clusters of germanium (Ge_5 to Ge_9) the electron affinity was estimated from the photoelectron spectrum measured at 266 nm following the method outlined by Xu *et al.*[8] in their study of small indium phosphide clusters. The electron affinity is determined from the measured binding energy spectrum by extrapolating the lin-

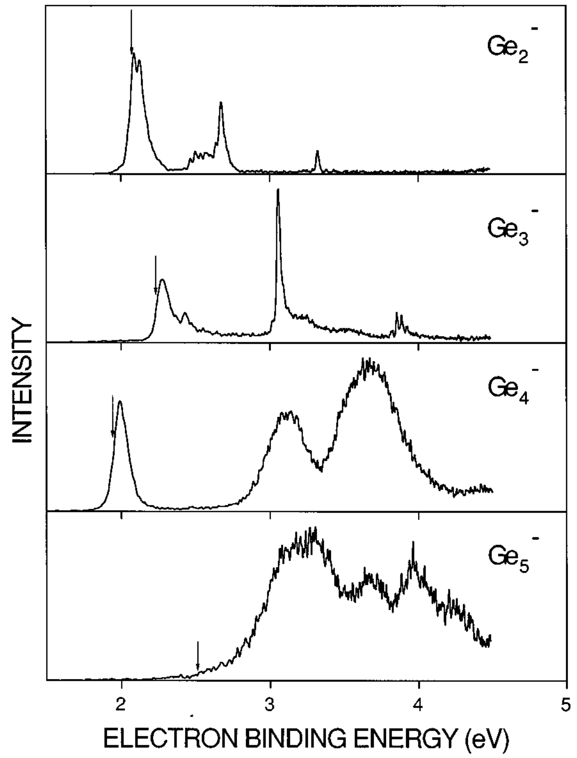

FIG. 4. Anion photoelectron spectra of Ge_n^-, $n=2-5$ measured using an incident laser wavelength of 266 nm. The spectra of Ge_2^- and Ge_3^-, and Ge_4^- and Ge_5^-, are reported at laser polarizations of 55° and 90°, respectively. The vertical arrow indicate the positions of the electron affinities determined in the present work.

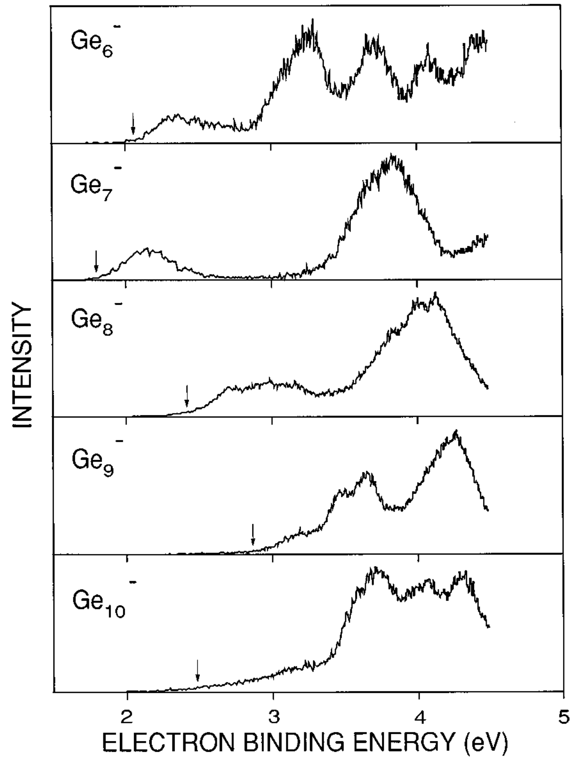

FIG. 5. Anion photoelectron spectra of Ge_n^-, $n=6-10$, measured using an incident laser wavelength of 266 nm. The spectra were measured using a laser polarization of 55°. The vertical arrows indicate the positions of the electron affinities determined in the present work.

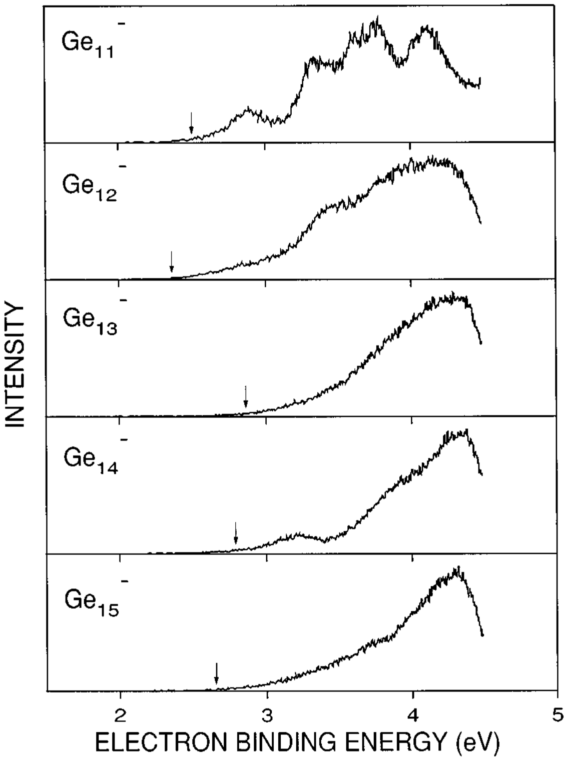

FIG. 6. Anion photoelectron spectra of Ge_n^-, $n=11-15$, measured using an incident laser wavelength of 266 nm. The spectra were measured using a laser polarization of 55°. The vertical arrows indicate the positions of the electron affinities determined in the present work.

ear portion of the first leading edge in the photoelectron spectrum to the energy axis. The point where this line crosses the axis is a reasonable estimate of the adiabatic electron affinity in the absence of well-resolved vibrational structure. Using this method, the electron affinities thus obtained are estimated to be accurate to ±50 meV. For $n \geqslant 10$, the spectra rise very slowly near the detachment threshold, making the determination of the electron affinities for these systems even more difficult. Since hot band excitation is certainly

TABLE I. Measured electron affinities for the germanium clusters studied in the present work. For $n=4-9$, the results have an uncertainty of ±0.05 eV, and for $n=10-15$, the uncertainty is ±0.1–0.2 eV.

Cluster	Electron affinity (eV)	Cluster	Electron affinity (eV)
Ge_2	2.035±0.001[a]	Ge_9	2.86
Ge_3	2.23±0.01[b]	Ge_{10}	2.5
Ge_4	1.94	Ge_{11}	2.5
Ge_5	2.51	Ge_{12}	2.4
Ge_6	2.06	Ge_{13}	2.9
Ge_7	1.80	Ge_{14}	2.8
Ge_8	2.41	Ge_{15}	2.7

[a] Electron affinity for Ge_2 determined from the energy of the ${}^3\Sigma_g^-(X0_g)(v'=0)\leftarrow{}^2\Pi_u(3/2)(v''=0)$ transition obtained from the ZEKE photoelectron work of Arnold *et al.* (Ref. 15).

[b] Electron affinity for Ge_3 determined from the estimated energy of the ${}^3A_2'(v'=0)\leftarrow{}^2A_1(v''=0)$ transition.

present, the electron affinities for these largest clusters must be viewed with caution. We estimate error bars to be ±0.1–0.2 eV.

B. Germanium dimer (Ge_2)

The photoelectron spectrum of Ge_2^- obtained at incident laser wavelength of 416 and 266 nm are shown in Figs. 1(a) and 1(b). The 416 nm spectrum has been fully described by Arnold *et al.*[15] in conjunction with much higher resolution measurements made using zero electron kinetic energy (ZEKE) spectroscopy. The 266 nm spectrum was not reported previously.

The 266 nm photoelectron spectrum of Ge_2^- consists of three distinct bands beginning at binding energies of 2.1, 2.6, and 3.32 eV. The two lower energy bands are much better resolved in the 416 nm spectrum as a consequence of the energy resolution degrading as $(\mathrm{eKE})^{3/2}$. As discussed in Ref. 15, the band at 2.1 eV is assigned to transitions from the $X\ {}^2\Pi_u$ and ${}^2\Sigma_u^+$ states of Ge_2^- to the two nearly degenerate $X\ {}^3\Sigma_g^-$ and $A\ {}^3\Pi_u$ triplet states of Ge_2, and the band at 2.6 eV corresponds to transitions to the $a\ {}^1\Delta_u$, $b\ {}^1\Sigma_g^+$, and $c\ {}^1\Pi_u$ singlet states. The band at 3.32 eV consists of a single peak and is too high in energy to be seen in the 416 nm spectrum. Based on the electronic structure calculation by Balasubramanian[26,27] this is assigned to the $d\ 2\ {}^1\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ transition. From the term energy of the ${}^2\Sigma_u^+$ state of Ge_2^-, 0.035 eV, and the electron affinity of Ge_2, 2.035 eV (both from Ref. 15), the photoelectron spectrum fixes T_e for the $d\ 2\ {}^1\Sigma_g^+$ state of Ge_2 at 1.32 eV, in excellent agreement with the calculated value of 1.34 eV.

C. Germanium trimer (Ge_3)

The photoelectron spectra of Ge_3^- measured at 416, 355, and 266 nm are shown in Figs. 2(a)–2(c). The 266 nm spectrum[2] of Si_3^- is shown for comparison in Fig. 2(d). In the Ge_3^- spectra, at least five bands are apparent with origins at binding energies of 2.23, 2.44, 3.04, 3.2, and 3.83 eV. The overall intensity profile of the band beginning at 2.23 eV changes as the laser polarization angle is rotated at 416 and 355 nm (not shown). As in previous studies,[45] this indicates that this feature consists of two overlapping neutral←anion electronic transitions, labeled X and A in Fig. 2(a). The remaining bands are labeled from B–E. Bands (X,A), B, and E show associated vibrational progressions with frequencies of 150, 355, and 266 cm^{-1}, respectively. In addition, there is a small peak that lies 290 cm^{-1} below the band E origin which is presumably a hot band transition from vibrationally excited Ge_3^-.

Theoretical studies of Ge_3 indicate[35,36] that the ground electronic state of the molecule is ${}^1A_1$ in C_{2v} symmetry with a low-lying, nearly degenerate, ${}^3A_2'$ state of D_{3h} symmetry. The leading orbital configuration of Ge_3 in C_{2v} symmetry has been determined by Dai *et al.*[35] to be $\ldots(a_1)^2(b_1)^2(b_2)^2(a_1)^0({}^1A_1)$. The ground electronic state of the anion, as in Si_3^-, is therefore expected to be $\ldots(a_1)^2(b_1)^2(b_2)^2(a_1)^1({}^2A_1)$. In addition to the low-lying ${}^1A_1$ and ${}^3A_2'$ states of Ge_3, Dai *et al.* predict that there are four excited states, the ${}^1B_2$, ${}^3B_1$, ${}^3A_1$, and ${}^1B_1$, states, that are accessible from the ground electronic state of the ion at 4.66 eV photon energy. Two other states that are energetically accessible, the ${}^3A_2$ and ${}^1A_2$ states, cannot be accessed from the anion ground state via one-electron transitions and are therefore unlikely to be seen in our experiment. Thus, six states of Ge_3 are predicted, and this matches the number of bands that are seen in our spectrum.

The actual assignment of the Ge_3^- photoelectron spectrum is facilitated by its remarkable similarity to that of Si_3^-. Thus recent calculations,[9,36] anion photoelectron spectroscopy[2] and ZEKE experiments[7] on Si_3^- can be used to advantage. The lowest energy band of the Si_3^- photoelectron spectrum shows a resolved vibrational progression with a frequency of 360±40 cm^{-1}. Analysis of the higher resolution ZEKE spectrum showed that this is a progression in the degenerate e' mode of the ${}^3A_2'$ state of Si_3; Dixon and Gole[36] predict this frequency to be 322 cm^{-1}, and Fournier *et al.*[46] calculate a frequency of 340 cm^{-1}. This mode is active only because of Jahn–Teller effects in the ${}^2A_1$ state of Si_3^-; this appears to be a fluxional species with a low barrier to pseudorotation.[7] A comparison of the ZEKE and photoelectron spectra indicates that transitions to the ${}^1A_1$ state of Si_3 overlap the triplet band, but no vibrational structure associated with the singlet transition is resolved. This absence of structure probably occurs because the calculated bond lengths and angle for the anion[9] ($\theta=65.2°$, $R_e=2.261$ Å) are quite close to the equilateral geometry of the ${}^3A_2'$ state ($R_e=2.290$ Å) but very different from that of the ${}^1A_1$ state ($\theta=79.6°$, $R_e=2.191$ Å). One therefore expects transitions to highly vibrationally excited levels of the ${}^1A_1$ state where considerable spectral congestion would be expected.

In the case of Ge_3, the e' vibrational frequency for the ${}^3A_2'$ state is calculated[36] to be 157 cm^{-1}, in excellent agreement with the observed spacing of 150 cm^{-1} in band (X,A) in Fig. 2(a). It therefore appears that the vibrational structure in this band is from the ${}^3A_2' \leftarrow {}^2A_1$ transition, implying that Jahn–Teller coupling is important in the anion ${}^2A_1$ state. As mentioned above, two overlapping transitions contribute to this band, so we assign the other to the ${}^1A_1 \leftarrow {}^2A_1$ transition. No vibrational structure from the latter transition is apparent. Although the Ge_3^- geometry has not been calculated, the calculated[35] geometry for the ${}^1A_1$ state Ge_3 is $R_e=2.294$ Å, $\theta=83.4°$, which, as in Si_3, is quite different from the ${}^3A_2'$ geometry ($R_e=2.457$ Å, $\theta=60°$). Hence, as in the Si_3^- photoelectron spectrum, we are probably accessing a highly congested manifold of vibrational levels of the ${}^1A_1$ state. If the ${}^3A_2'$ state is the ground state of Ge_3, then its electron affinity is given by the origin of the (X,A) band, 2.23±0.010 eV. However, it is possible that the ${}^1A_1$ state is the ground state, but that the anion has negligible Franck–Condon overlap with the $v=0$ level of this state, in which case the above value represents an upper bound to the true electron affinity.

We next consider the higher energy bands. Based on the comparison with the Si_3^- spectrum, bands B–E should be assigned to transitions to the ${}^1B_2$ ($T_0=0.21$ eV), ${}^3A_1$ (0.81 eV), ${}^3B_1$ (1.0 eV), and ${}^1B_1$ (1.69 eV) states, respectively, of Ge_3, where the experimental term energies are relative to the

$^3A_2'$ state. The excited state Si_3 assignments[9] were based on a comparison of experimental and calculated term energies, and on a comparison of the calculated anion and neutral geometries with the experimental Franck–Condon profiles. For example, the band at 3.3 eV in Fig. 2(d) contains only a single peak, indicating that the geometry of the neutral and anion are very similar, and the assignment of this feature to the $^3A_1$ state is consistent with this. The trends in calculated geometries[35] amongst the Ge_3 excited states are similar to those for Si_3, so given the similarity between the spectra, it is certainly reasonable that the same assignments apply. However, the calculated energy ordering and term values for the Ge_3 states are somewhat different than what we find experimentally. For example, the $^3A_1$ state is calculated to lie 0.18 eV above the $^3B_1$ state, whereas we find approximately the same splitting with the opposite state ordering. Also, while the $^1B_1$ state is calculated to be the highest of the group, its calculated term energy is only 1.07 eV vs the experimental value of 1.69 eV. Nonetheless, the overall agreement between experiment and theory is quite good, given the complexity of this species.

D. Germanium tetramer (Ge_4)

The anion photoelectron spectra of Ge_4^- at 4.66 eV (266 nm) and 3.49 eV (355 nm) are shown in Figs. 3(a) and 3(b), respectively. For comparison, the spectrum of Si_4^- measured by Kitsopoulos *et al.*[2] at 3.49 eV is shown in Fig. 3(c). Figure 3(a) shows that there are three distinct bands in the photoelectron spectrum of Ge_4^-, at binding energies of 2.0, 2.8, and 3.7 eV. From Figs. 3(b) and 3(c), it is clear that the spectra of Ge_4^- and Si_4^- are very similar. Furthermore, the spectrum of Si_4^- measured at 4.66 eV by Kitsopoulos *et al.*[2] (not shown) is also qualitatively similar to the spectrum of Ge_4^- shown in Fig. 3(a). However, the Si_4^- spectrum measured at 3.49 eV [Fig. 3(c)] shows distinct vibrational structure in both bands present in that spectrum, whereas no resolved vibrational structure is seen in either band of the 3.49 eV Ge_3^- spectrum. The inset in Fig. 3(b) shows the ZEKE spectrum of part of the 2.8 eV band. This higher resolution spectrum shows vibrational structure with a characteristic frequency of 173 cm^{-1}, but the peaks are quite broad in the ZEKE spectrum, indicating that there is some excitation in the low-frequency vibrational modes of the Ge_4^- anion. Such excitation was observed in the ZEKE spectrum[6] of Si_4^-, but in that case it was possible to resolve the individual hot bands and sequence bands; the lower frequencies in Ge_4^- and Ge_4 make this more difficult.

Calculations[29,33,34] on Ge_4 indicate that its ground state is a planar rhombus of D_{2h} symmetry with electronic symmetry ^1A_g, just as for Si_4. Although no calculations have been done on the Ge_4^- anion, Si_4^- has a $^2B_{2g}$ ground state;[9] this is also a planar rhombus with a geometry quite close to that of the Si_4 ground state, as evidenced by the narrow Franck–Condon profile in the lowest energy band of the Si_4^- photoelectron spectrum. This band is also very narrow in the Ge_4^- photoelectron spectrum, implying that it, too, is from the $^1A_g \leftarrow {}^2B_{2g}$ transition between two states with similar geometries.

Dai and Balusubramanian[34] have calculated vertical excitation energies (but not geometries) for several excited states of Ge_4. They find the first excited state to be the $^3B_{3u}$ state, at a vertical excitation energy of 1.41 eV above the ^1A_g state. This suggests that the second band in Fig. 3(b) is the $^3B_{3u} \leftarrow {}^2B_{2g}$ transition, which would be consistent with the assignment of the analogous band in the Si_4^- photoelectron spectrum. The Si_4^- ZEKE spectrum[6] of this band shows an extended vibrational progression at 312 cm^{-1}, assigned to the a_1 "breathing" mode of Si_4. A long progression in this mode is consistent with the calculated geometry change[9] between the Si_4^- $^2B_{2g}$ state and the Si_4 $^3B_{3u}$ state; the latter is also a planar rhombus, but is less elongated than the anion. In the case of Ge_4, the 173 cm^{-1} progression seen in the ZEKE spectrum of this band is also most likely in the breathing mode of Ge_4; if the value of 312 cm^{-1} for Si_4 is scaled by $\sqrt{m_{Si}/m_{Ge}}$, a frequency of 194 cm^{-1} is predicted for this mode in Ge_4. Hence, the same type of geometry change between the anion and neutral is presumably occurring in this band of the Ge_4^- spectrum.

E. Larger germanium clusters (Ge_5–Ge_{15})

The photoelectron spectra of Ge_n^-, $n=5-15$ measured at a photon energy of 4.66 eV (266 nm) are shown in Figs. 4–6; the spectra of the $n=2-4$ clusters are included for completeness. In general, the spectra for $n \geqslant 5$ are significantly broader than those of the smaller clusters and indicate the presence of multiple electronic transitions. These spectra are similar to those obtained by Cheshnovsky *et al.*[11] in that no vibrational structure is resolved. However, the electronic bands are better separated in several of our spectra, and we have spectra for $n=13-15$ that were not reported previously.

The arrows on the figures indicate the positions of the estimated electron affinities for the germanium clusters determined in the present work and these are given in Table I. For the clusters with $n \leqslant 9$, the electron affinities in Table I are in reasonable agreement with Cheshnovsky's values. The largest disagreement is for Ge_3 (2.23 vs 1.9 eV in Ref. 11). Also, we measure a larger difference in EA(Ge_6)–EA(Ge_7): 0.26 vs 0.1 eV.

The other noteworthy feature in several of these spectra is the presence of a sizeable gap between the first and second electronic bands, representing a large spacing between the ground and first excited electronic state of the neutral cluster. This is most prominent in the Ge_4^- and Ge_7^- spectra, as was seen by Cheshnovsky. A less pronounced gap is evident in the Ge_6^- spectrum. The electron affinities of Ge_4, Ge_6, and Ge_7 are noticeably lower than those of the neighboring clusters. In the Ge_{11}^- and Ge_{14}^- spectra one observes a broad peak near the detachment threshold, in contrast to the neighboring $(n \pm 1)$ spectra where only a smoothly rising signal is seen.

The significance of patterns in the variation of electron affinities with cluster size and the presence of electronic gaps has been discussed previously with reference to clusters of carbon,[1,47] gallium arsenide,[48] and indium phosphide.[8] For the linear carbon clusters ($n \leqslant 9$), those with an even number of atoms have a greater electron affinity than those with an odd number. This occurs because the odd clusters have closed-shell, ${}^1\Sigma_g^+$ ground states, so that the additional electron in the anion must occupy a relatively high-lying orbital, whereas the even clusters have open-shell ${}^3\Sigma_g^-$ ground states, and the additional electron can then go into a half-occupied, low-lying orbital. In $\mathrm{Ga}_x\mathrm{As}_y$ and $\mathrm{In}_x\mathrm{P}_y$ clusters, the even clusters, regardless of stoichiometry, have lower electron affinities than odd clusters of comparable size. Moreover, the photoelectron spectra of even cluster $\mathrm{In}_x\mathrm{P}_y^-$ show a sizeable electronic gap which is absent for the odd clusters. These trends can be explained by assuming that the even clusters are closed-shell species with substantial HOMO-LUMO gaps. The additional electron in the anion then must occupy a relatively high-lying orbital and the electronic gap in the anion photoelectron spectrum is essentially the HOMO-LUMO splitting in the neutral cluster. In contrast, the odd $\mathrm{In}_x\mathrm{P}_y$ clusters have an odd number of electrons, and are therefore open-shell species with high electron affinities.

Neutral Si_n and Ge_n are like carbon clusters in that they have an even number of electrons regardless of n, but the pattern of the electron affinities is not nearly so clear as the even–odd alternation seen for carbon clusters. Of the spectra presented here, those for Ge_4^- and Ge_7^- most clearly resemble the photoelectron spectra of $\mathrm{In}_x\mathrm{P}_y^-$ clusters with an even number of atoms, implying that Ge_4 and Ge_7 are closed-shell species with large HOMO-LUMO gaps. This is consistent with our previous discussion of the electronic states of Ge_4, and also with *ab initio* calculations by Pacchioni and Koutecky[31] on Ge_7. These predict a pentagonal bipyramid geometry (D_{5h} symmetry) with a ${}^1A_1'$ ground state and ${}^3E''$ first excited state lying 1.89 eV higher. No calculations have been performed on Ge_7^-, but Si_7^- is also predicted to be a pentagonal bipyramid with a ${}^2A_2''$ ground state.[49] Assuming Ge_7^- has the same symmetry and electronic configuration, then both the ${}^1A_1'$ and ${}^3E''$ states of Ge_7 are accessible via one-electron transition (removal of an electron from an a_2'' or e' orbital, respectively), and the electronic gap in our spectrum, ~1.8 eV, agrees well with the calculated splitting. We therefore assign the first and second bands to transitions to the ${}^1A_1'$ and ${}^3E''$ states of Ge_7.

The situation with Ge_6 is more ambiguous. Its electron affinity is almost as low as that of Ge_7, but more bands are evident in the spectrum, and the gap between the first two bands (~1.0 eV) in the Ge_6^- spectrum is significantly smaller than in the Ge_7^- spectrum. Pacchioni[31] predicts an tripyramidal (C_{2v}) geometry for Ge_6 with a ${}^1A_1$ ground state, and a ${}^3B_2$ excited state (also C_{2v}) lying 1 eV higher. If the anion is tripyramidal with a ${}^2B_2$ ground state, then Pacchioni's calculation supports assigning the first two bands in the Ge_6^- spectrum to the ${}^1A_1$ and ${}^3B_2$ states. However, Raghavachari's most recent calculations[10,49] predict tetragonal bipyramidal D_{4h} structures for Si_6 and Si_6^- with ${}^1A_{1g}$ and ${}^2A_{2u}$ ground states, respectively. Results for this point group were not reported by Pacchioni. Raghavachari's ground state Si_6 structure is supported by the experimental Raman spectrum of Si_6.[10] Assuming his results for Si_6 and Si_6^- can be applied to Ge_6 and Ge_6^-, then the first two bands in the photoelectron spectrum may be due to transitions to the ${}^1A_{1g}$ ground state and a low-lying triplet state, most likely a ${}^3E_g$ state formed by removal of an electron from the highest occupied e_u orbital (the HOMO in Si_6).[50] Further calculations on Ge_6 and/or experimental Raman spectroscopic investigations may be needed to resolve these two interpretations of the photoelectron spectrum.

While a low electron affinity and large electronic gap should generally be a signature of a closed-shell cluster, the interpretation of photoelectron spectra that do not display these attributes is more complex. As an example, consider the Ge_5^- photoelectron spectrum. This spectrum shows that the electron affinity of Ge_5 is relatively high, 2.51 eV, and that the splitting between the first two bands is only 0.5 eV. Pacchioni[31] finds the open-shell ${}^3A_2'$ trigonal bipyramid (D_{3h}) state to be the ground state of Ge_5. However, Raghavachari's calculations on silicon pentamers predict a ${}^1A_1'$ closed-shell D_{3h} structure to be the ground state, with the ${}^3A_2'$ state lying 1 eV higher.[51] He also finds a ${}^3B_1$ excited state in C_{2v} symmetry that lies 0.5 eV above the ground state, and a D_{3h} trigonal bipyramid ground state for Si_5^-, a ${}^2A_2''$ state.[49,50] The C_{2v} geometry represents only a slight distortion of a trigonal bipyramid. The ${}^1A_1'$ and ${}^3B_1$ states are accessible from the anion, whereas the ${}^3A_2'$ state is not. Based on Raghavachari's calculations, one would assign the first two bands in the Ge_5^- spectrum to transitions to the analogous ${}^1A_1'$ and ${}^3B_1$ states in Ge_5. This assignment suggests that the difference between Ge_5 and Ge_7 is not that one species has an open-shell and one closed-shell ground state, but rather that the closed-shell ground state of Ge_7 represents a particularly stable electronic configuration, whereas the HOMO-LUMO gap in Ge_5 is relatively small.

For the larger clusters, the photoelectron spectra of Ge_{11}^- and Ge_{14}^- are most consistent with closed-shell neutral clusters. No *ab initio* calculations have been performed on either species. While structures have been obtained using model potentials,[32,37] the results of these calculations are somewhat suspect since they disagree with the *ab initio* results for many of the smaller ($n \leqslant 10$) clusters. *Ab initio* calculations using an effective core potential[52] have been carried out for Si_{11} and predict two rather close lying states (within 6 kcal/mol), albeit with quite different geometries. Overall, theory provides little help in interpreting either of these spectra.

In much of the above discussion, we have interpreted the Ge_n^- spectra with the aid of calculations on Si clusters. This is partly due to necessity, but also appears justified because the photoelectron spectra of Si_n^- and Ge_n^- presented here and in Ref. 11 are usually quite similar. The one notable exception is for the $n=10$ clusters. The Si_{10}^- photoelectron spectrum[11] indicates that Si_{10} has a low electron affinity and a large electronic gap, indicating that Si_{10} is a stable, closed-shell species. This is supported by calculations of the incremental atomic binding energies, $E_n - E_{n-1}$, for Si clusters, which is particularly large for Si_{10} (along with Si_4, Si_6, and Si_7).[52] However, there is no evidence for a comparable electronic gap in the Ge_{10}^- spectrum. This could be due to differing geometries and/or electronic configurations in either the neutral or anion clusters, and we hope that future *ab initio* calculations on these species can resolve this issue.

IV. CONCLUSIONS

Using a combination of anion photoelectron and ZEKE spectroscopy, we have mapped out vibrationally resolved electronic states of Ge_{2-4}. The spectra are remarkably similar to those of the corresponding Si clusters, thereby aiding considerably in their interpretation. For the larger ($n = 5-15$) clusters, no vibrational structure is resolved in the photoelectron spectra, but electronic bands are clearly observed. With the aid of *ab initio* calculations, these can be assigned in some cases. The spectra clearly indicate that Ge_4, Ge_7, and, to a lesser extent, Ge_6 are closed-shell species with substantial HOMO-LUMO gaps. There is also evidence that this is the case for Ge_{11} and Ge_{14}, but not Ge_{10}.

The assignment of the features in the spectra of the larger clusters would be greatly facilitated if vibrational structure could be resolved. Although the absence of structure is partly due to the resolution of the spectrometer (~10 meV), further cooling of the cluster anions would help considerably. We have recently developed a pulsed discharge source that makes considerably colder Si cluster anions than the laser ablation source used here, and it will be of considerable interest to generate Ge_n^- clusters with this source and observe the effect on the photoelectron spectra. Such experiments are planned for the near future.

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