

STUDY OF SMALL SEMICONDUCTOR CLUSTERS USING ANION PHOTOELECTRON SPECTROSCOPY: GERMANIUM CLUSTERS (Ge_n , $n = 2-15$)

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The technique of anion photoelectron spectroscopy has been used at 266, 355, and 416 nm to study small germanium clusters, Ge_n^- , $n = 2-15$. The electron affinities for these cluster anions have been determined from the photoelectron spectra. The spectra for Ge_2^- and Ge_3^- show well-resolved vibrational structure.

1. Introduction

The technique of anion photoelectron spectroscopy has been used to great advantage in recent work for studying small elemental clusters of carbon¹⁻³ and silicon.⁴⁻⁶ In addition, zero-electron-kinetic-energy (ZEKE) spectra for these systems⁶⁻¹⁰ have proven essential for the elucidation of the spectral assignments. One motivation for these studies is to determine how the electronic properties of a semiconducting element changes as the size of the system under study is increased from a single atom to the bulk solid.

There have been numerous theoretical studies of small germanium clusters aimed at determining electronic properties for Ge_2^{11-23} and the most stable geometric configuration, as well, for Ge_3 – Ge_6 .^{19,22,24-29} The results available as of 1990 have been summarized by Balasubramanian.³⁰

In contrast to the numerous calculations on small germanium clusters, there exist only a limited number of experimental studies of these systems.^{4,31,32} The work of Froben and Schulze³¹ and of Li *et al.*³² were aimed at determining vibrational frequencies for electronic states of Ge_2^- in rare-gas matrices. The photoelectron spectra of germanium clusters (Ge_n^- , $n = 3-12$) have been measured by Cheshnovsky *et al.*⁴ over a wide photoelectron kinetic energy range using an incident photon beam of 6.4 eV, at a modest resolution.

In the present study we now report photoelectron spectra for Ge_n^- , $n = 2-15$, measured at wave-

lengths of 266, 355, and 416 nm. The electron affinities for these cluster anions have been determined from the measured anion photoelectron spectra. The resolution of the present technique (~ 10 meV) is better than that available to Cheshnovsky *et al.*⁴ (~ 150 meV). This is important for the lower mass clusters (Ge_3^- , Ge_4^-) where significant spectral differences were observed.

2. Experimental

The photoelectron spectrometer used to make the measurements reported in the present work has been described in detail previously,³³ so only a brief description will be given here.

Germanium clusters were produced by focusing the output of a Nd:YAG laser (532 nm, $\sim 5-10$ mJ/pulse) onto a rotating and translating rod of germanium (ESPI, stated purity of 99.9999%) in a cluster source similar in design to that reported previously.³⁴ The resulting plasma was entrained in a supersonic expansion of a noble-gas carrier and then underwent a soft expansion into the vacuum chamber. The negative ions thus formed were admitted into a Wiley–McLaren-type³⁵ mass spectrometer and were separated according to their mass-to-charge ratio by time-of-flight. The resolution ($m/\Delta m$) of this instrument is about 250 and was found to be sufficient to resolve the individual isotope peaks for all clusters of mass less than or equal to that of Ge_4^- . A pulse from a second (higher power) Nd:YAG laser was timed so as to intercept the cluster ion of interest, and the

energies of the resulting photoelectrons were determined by their flight times in a calibrated time-of-flight tube. The three photodetachment laser wavelengths used were the fourth (266 nm, 4.66 eV) and third (355 nm, 3.49 eV) harmonics of the Nd:YAG, and the 416-nm (2.98-eV) laser light was produced by Raman-shifting the third harmonic by passage through a high-pressure cell containing hydrogen. The spectra of Ge_2^- , Ge_3^- , and Ge_4^- were measured at mass-to-charge ratios of 146, 218, and 291, respectively. For the higher mass clusters the laser was timed to photodetach at the maximum of the ion-cluster distribution. Spectra for Ge_2^- and Ge_3^- were measured at polarization angles (i.e., the angle between the plane of polarization of the laser and the direction of the detected electrons) of 0° and 90° . The spectra for the other germanium anions (Ge_n^- , $n = 4-15$) were measured at a polarization of 55° . The photoelectron spectra have been smoothed with a Gaussian function (6-meV FWHM) to reduce random noise in the spectra.

3. Results and Discussion

The photoelectron spectra measured in the present work for Ge_n^- , $n = 2-15$, are shown in Figs. 1-5. The kinetic energy of the ejected electron, eKE , is related to the internal energy of the neutral molecule by

$$eKE = h\nu - EA - T_0^0 + T_0^- - E_v^0 + E_v^- \quad (1)$$

In Eq. (1), $h\nu$ is the laser energy, EA is the electron affinity of the neutral species, T_0^0 and T_0^- are the term values of the specific neutral and anion electronic states, respectively, and E_v^0 and E_v^- are the vibrational energies (above the zero-point energy) of the neutral and anion, respectively. It can be seen from Eq. (1) that peaks occurring at lower electron kinetic energies correspond to states of higher internal energy in the neutral molecule.

The resolution of the present spectrometer has been found to be 8-meV FWHM at an electron kinetic energy, eKE , of 0.65 eV and degrades as $(eKE)^{3/2}$ with increasing electron kinetic energy. The resolution was sufficient to resolve individual vibronic peaks in the spectrum of Ge_2^- and Ge_3^- and has resolved additional bands in higher mass clusters which were not apparent in the spectra reported by Cheshnovsky *et al.*⁴

In general, for any photodetachment (or photoionization) process the angular distribution of ejected photoelectrons, $d\sigma/d\theta$, is related to the polarization angle, θ , by

$$\frac{d\sigma}{d\theta} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 + \frac{\beta}{2}(3 \cos^2 \theta - 1) \right], \quad (2)$$

where σ_{total} is the total cross section integrated over all angles, and β is the so-called beta parameter and is (essentially) constant for a given electronic transition. Thus, it can be deduced from Eq. (2) that if the polarization angle is varied then the observed spectral intensities for different electronic states will vary because of their differing β values. However, spectral lines associated with the same electronic transition (e.g., vibronic transitions) have the same β parameter and will thus increase, or decrease, proportionally.

The presently measured anion photoelectron spectra for Ge_2^- are shown in Figs. 1 and 3 at photon energies of 416 and 266 nm, respectively. Figure 3

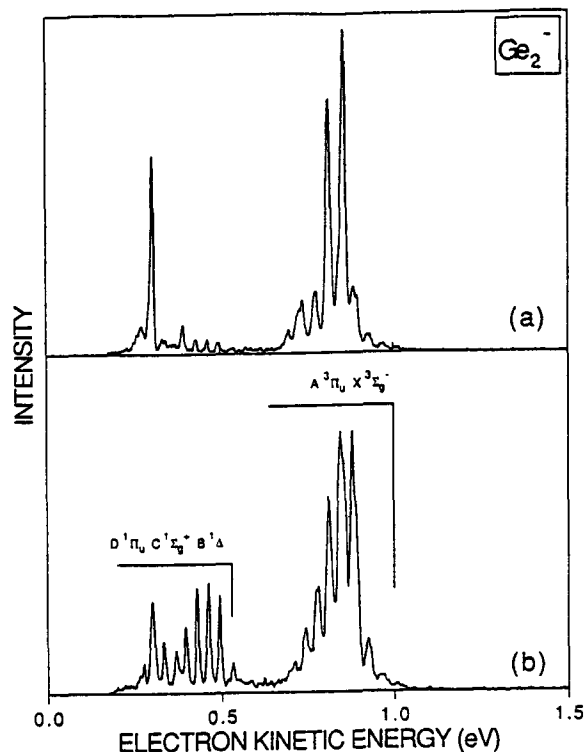


Fig. 1. Anion photoelectron spectra of Ge_2^- measured using 416-nm incident radiation. (a) Polarization angle of 0° . (b) Polarization angle of 90° .

shows that the spectrum consists of essentially three bands of overlapping electronic transitions at electron kinetic energies of 2.5, 2.0, and 1.3 eV. The bands at 2.0 and 2.5 eV are shown at higher resolution in Fig. 1. Figures 1(a) and 1(b) show that these bands have a significant polarization dependence and are composed of multiple electronic transitions.

The outermost valence-shell orbitals of Ge_2 have, in a one-electron approximation, σ_g and π_u symmetry. The electronic configuration of the outermost electrons in Ge_2 can be $(\sigma_g)^2(\pi_u)^2$, which gives rise to the electronic states $^1\Sigma_g^+$, $^3\Sigma_g^-$, and $^1\Delta_g$, or $(\sigma_g)^1(\pi_u)^3$, which gives $^1\Pi_u$ and $^3\Pi_u$, or $(\sigma_g)^0(\pi)^4$, which yields a second $^1\Sigma_g^+$ state. The electronic configuration of the germanium-dimer anion is obtained by adding an electron to a vacant orbital on the neutral dimer and can be $(\sigma_g)^2(\pi_u)^3$, which corresponds to $^2\Pi_u$ or $(\sigma_g)^1(\pi_u)^4$, which corresponds to an electronic state of $^2\Sigma_g^+$. The spectra in Fig. 1 can be seen to be composed of two bands centered at electron kinetic energies of about 0.8 and 0.4 eV. These correspond to transitions from the ground states of the anion to the triplet states ($X^3\Sigma_g^-$, $A^3\Pi_u$) and singlet states ($B^1\Delta_g$, $C^1\Sigma_g^+$, $D^1\Pi_u$) of Ge_2 , respectively. A detailed analysis of these transitions has been made in light of recent threshold photodetachment (ZEKE) experiments of Ge_2^- and is reported elsewhere.³⁶ By increasing the incident photon energy, a wider range of internal electronic states of the neutral molecule can be accessed [see Eq. (1)] at a loss of resolution of the spectral features at high electron kinetic energy. For example the resolution for corresponding peaks in the spectrum of Ge_2^- shown in Fig. 1 is much higher than that presented in Fig. 3; however transitions to the $E^1\Sigma_g^+$ state (at an electronic kinetic energy of about 1.3 eV in the top panel of Fig. 3) are absent in Fig. 1.

The anion photoelectron spectrum of Ge_3^- measured at 266 nm is shown in Fig. 3. At least six electronic states can be identified in the spectrum and these have been labeled X , A , B , C , D , and E . The anion photoelectron spectra for Ge_3^- measured in the present work at a polarization of 90° are shown in Figs. 2(a) and 2(b), and were obtained using photon energies of 355 and 416 nm, respectively. It is interesting to note that the measured spectrum for Ge_3^- obtained at 416 nm in the present work is very similar to the corresponding spectrum of Si_3^- measured previously from this laboratory.⁵ The X band

shows a resolved progression of at least five peaks with an average spacing of ~ 0.019 eV (150 cm^{-1}) and the band labeled B has a vibrational progression with an average spacing of 0.044 eV (355 cm^{-1}). The C band shows no vibrational progression and has a strong polarization dependence increasing in intensity at 0° (not shown in Fig. 2). It can be seen from Fig. 3 that the E band shows a vibrational progression with an average spacing of 0.033 eV (266 cm^{-1}).

The similarity of the spectra of Ge_3^- and Si_3^- can be used to elucidate the assignment of the Ge_3^- spectrum in light of recent calculations on Si_3^- .³⁷ Calculations^{28,29} on the Ge_3^- anion have shown that the lowest energy configuration is bent and has C_{2v} symmetry. The symmetry of the ground electronic state is 1A_1 , with a close-lying state of 3A_2 (D_{3h}) symmetry [$^3B_2(C_{2v})$].²⁹ The band at an electron kinetic energy of ~ 1.2 eV [see Fig. 2(a)] therefore likely corresponds to overlapping transitions from the 2A_1 ground state of the anion to the X^3A_2' and A^1A_1

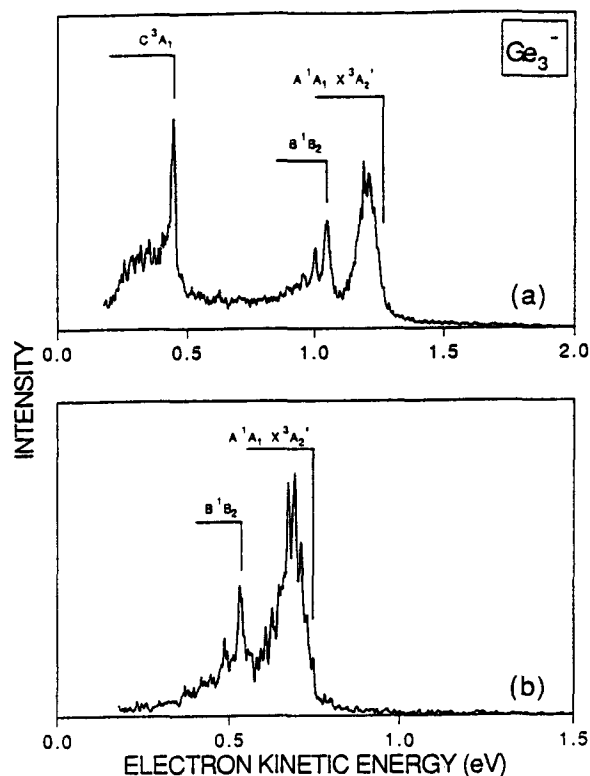


Fig. 2. Anion photoelectron spectra of Ge_3^- measured at a polarization angle of 90° . (a) Incident laser wavelength of 355 nm. (b) Incident laser wavelength of 416 nm.

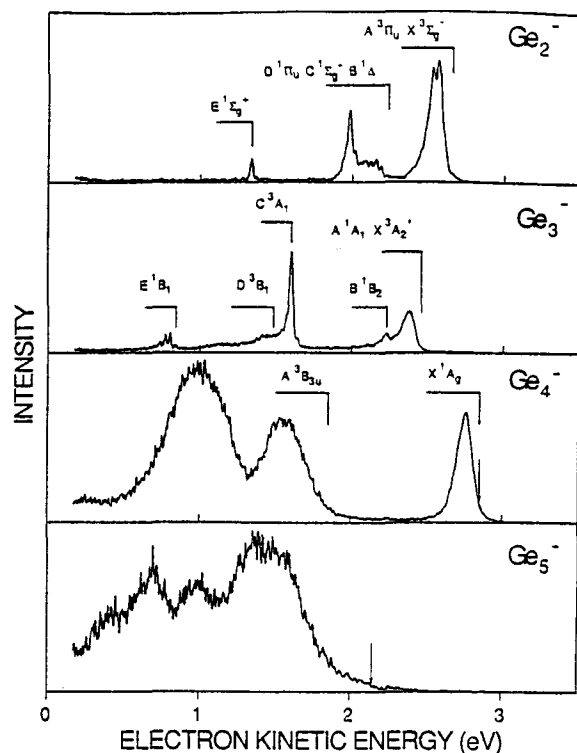


Fig. 3. Anion photoelectron spectra for germanium clusters, Ge_n^- , $n = 2-5$, measured using 266-nm incident radiation. The vertical arrows indicate the positions of the electron affinities determined in the present work. The spectra for Ge_2^- and Ge_3^- , and Ge_4^- and Ge_5^- were measured at laser polarizations of 55° and 90° , respectively.

states. The observed vibrational frequency of 150 cm^{-1} for the $X^3A'_2$ state agrees well with the asymmetric stretch frequency of 157 cm^{-1} calculated by Dixon and Gole.²⁸ Recent work on Si_3^- by Arnold and Neumark¹⁰ using threshold photodetachment (ZEKE) spectroscopy has determined that transitions to $X^3A'_2$ are present with a vibrational frequency of 337 cm^{-1} for the asymmetric stretch. Dai *et al.*²⁹ calculated that the 1B_2 state of Ge_3 lies about 0.4 eV above the ground state and this is assigned as band B. No calculated vibrational frequencies are available for this state. Following the assignment³⁷ of the photoelectron spectrum of Si_3^- the higher excited states C, D, and E are assigned as 3A_1 , 3B_1 , and 1B_1 , respectively.

The anion photoelectron spectrum of Ge_4^- shown in Fig. 3 consists of three bands at electron kinetic energies of 1.0, 1.6, and 2.8 eV. This spectrum is

qualitatively very similar to that of Si_4^- measured by Kitsopoulos *et al.*⁵ and has been assigned by Rohlfling and Raghavachari.³⁷ The most stable conformer of the Ge_4 cluster has been found to be a rhombus³⁸ with D_{2h} symmetry. The ground electronic and first excited state of Ge_4 have 1A_g and $^3B_{3u}$ symmetry, respectively. Thus, the bands labeled X and A likely correspond to transitions from the ground state of the Ge_4^- anion to the 1A_g and $^3B_{3u}$ states, respectively. The broad nature of the A band, and of the band at an electron kinetic energy of 1.0 eV (see Fig. 3), suggests that these bands are composed of transitions to multiple electronic states.

The electron affinities for the germanium cluster anions studied in the present work are indicated in Figs. 3-5 as vertical arrows and are given numerically in Table I. The present electron affinities are consistent with the photodetachment thresholds reported previously by Cheshnovsky *et al.*⁴ (except for

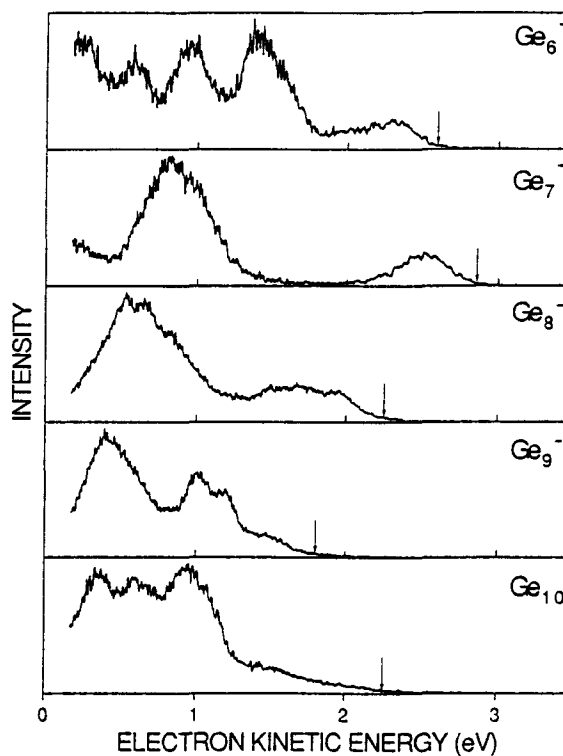


Fig. 4. Anion photoelectron spectra for germanium clusters, Ge_n^- , $n = 6-10$, measured using 266-nm incident radiation. The vertical arrows indicate the positions of the electron affinities determined in the present work. The spectra were measured at a laser polarization of 55° .

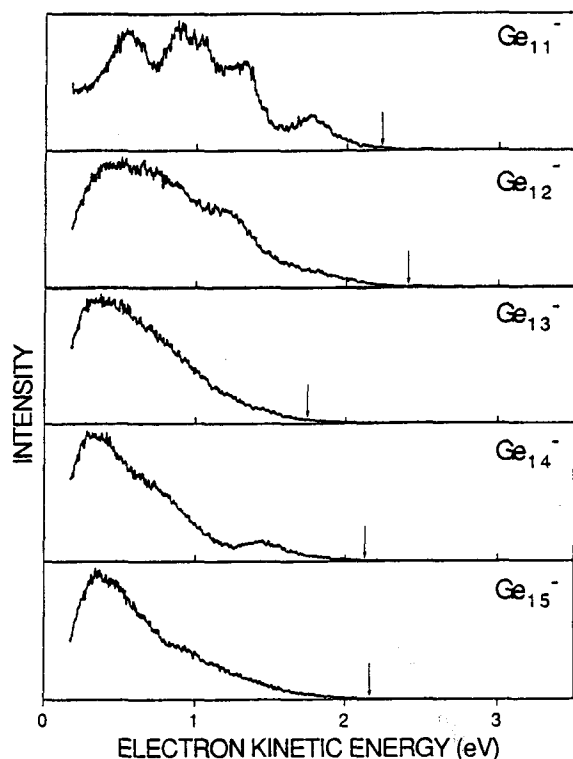


Fig. 5. Anion photoelectron spectra for germanium clusters, Ge_n^- , $n = 11-15$, measured using 266-nm incident radiation. The vertical arrows indicate the positions of the electron affinities determined in the present work. The spectra were measured at a laser polarization of 55° .

Table I. Measured electron affinities for the germanium clusters studied in the present work. The results have an estimated uncertainty of ± 0.05 eV.

Cluster ion	Electron affinity (eV)	Cluster ion	Electron affinity (eV)
Ge_2^-	2.074 ± 0.001^a	Ge_9^-	2.86
Ge_3^-	2.23 ± 0.01^b	Ge_{10}^-	2.41
Ge_4^-	1.81	Ge_{11}^-	2.43
Ge_5^-	2.51	Ge_{12}^-	2.25
Ge_6^-	2.06	Ge_{13}^-	2.91
Ge_7^-	1.80	Ge_{14}^-	2.53
Ge_8^-	2.41	Ge_{15}^-	2.50

^aElectron 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.³⁶

^bElectron affinity for Ge_3 determined from the energy of the $X^3A'_2(v' = 0) \leftarrow ^2A_1(v'' = 0)$ transition [see Fig. 2(b)].

Ge_3^- and Ge_4^- where thresholds of 1.9 and 1.9 eV were quoted) when differences in spectral resolution are considered. The present values have been determined by fitting a straight line to the leading edge at the highest electron kinetic energies. This procedure helps eliminate the contribution to the spectrum from transitions from vibrationally excited anions (hot bands). The first (low intensity) onset at high electron kinetic energies in each spectrum is attributable to hot bands. This is especially true for Ge_2^- because higher vaporization laser powers were used, compared with the other clusters, to produce sufficient quantities of this ion. Thus, the rising edge in the spectrum of Ge_2^- at an electron kinetic energy of ~ 2.6 eV is likely due to hot bands. The uncertainty in the present method of determining electron affinities is estimated to be better than ± 0.05 eV. The spectra for Ge_n^- , $n = 3-11$, are all better resolved in the present work than the corresponding spectra reported by Cheshnovsky *et al.*⁴ The improved resolution has shown evidence for new bands in the spectra of Ge_3^- , Ge_6^- , Ge_8^- , Ge_9^- , and Ge_{10}^- .

Acknowledgments

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