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Electron affinities of Ge and Sn

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The laser photoelectron spectra of Ge^- and Sn^- are reported. Transitions in the electron detachment from the $^4S_{3/2}$ ground state of the ions to the $^3P_{0,1,2}$ states of the neutral atom are used to determine the electron affinities, 1.233 ± 0.003 eV for Ge and 1.112 ± 0.004 eV for Sn. The relative transition strengths to the fine-structure sublevels of the neutral do not follow the 1:3:5 statistical ratio, indicating the systematic breakdown of *L*-*S* coupling for these species.

Laser-photodetachment experiments with atomic negative ions over the past 15 years have provided accurate electron affinities for most of the atoms in the periodic table, aside from the rare earths, but some gaps exist.[1] We report here photoelectron spectra of Ge^- and Sn^- which completes the determination of all Group-IVA electron affinities to within a few meV. These new electron affinities are in agreement with the earlier results of Feldmann, Rackwitz, Heinecke, and Kaiser[2] but are 35 times more accurate.

The negative ion photoelectron spectrometer[3,4] used in this work begins with a flowing afterglow ion source, from which ions are sampled, accelerated for mass selection, decelerated and crossed with the intracavity radiation of an Ar II laser operating at 488 nm (2.540-eV photons). Electrons photodetached in a direction perpendicular to both beams are energy analyzed in a hemispherical analyzer with resolution of approximately 10 meV FWHM. The absolute photoelectron energy calibration was determined by photodetaching O^-,[5] and the relative energy calibration from the known fine-structure intervals in the photodetachment spectrum of W^-.[6]

An 0.15-pA beam of $^{70}Ge^-$ was produced by the addition of GeH_4 gas downstream from a microwave discharge exciting a flow of helium [9 SLPM (standard liter per minute), 0.6 Torr] containing 0.03% O_2. A 4-pA beam of GeH_2^- was also obtained under these conditions (its photoelectron spectrum yields the electron affinity of GeH_2, 1.097 ± 0.015 eV). No evidence for GeH^- or GeH_3^- was seen in either the mass spectrum or photoelectron spectra. The Ge^- photoelectron spectra were obtained free of molecular contamination by selection of the low-mass isotope $^{70}Ge^-$.

An 0.7-pA beam of Sn^- was obtained by the addition of $(CH_3)_4Sn$ vapor downstream of the microwave discharge in a pure helium flow. Larger beam currents corresponding approximately to $Sn(CH_3)^-$, $Sn(CH_3)_2^-$, and $Sn(CH_3)_3^-$ were also observed. Inadequate mass resolution and the large number of stable Sn isotopes prevented us from obtaining Sn^- photoelectron spectra entirely free of molecular contamination.

The 488-nm Ge^- photoelectron spectrum is shown in Fig. 1. Transitions from the $4^4S_{3/2}$ ground state of Ge^- to the $4^3P_{0,1,2}$ fine-structure states of Ge are indicated in Fig. 1. The peak separations agree with the known[7] fine-structure intervals in $Ge(4^3P_{0,1,2})$ to within 0.3 meV. The electron affinity of Ge is determined to be 1.233 ± 0.003 eV from the photoelectron spectrum. Photoelectron spectra were obtained over the entire electron energy range accessible, 0.3–2.54 eV. No other transitions were observed, implying that no metastable excited states of Ge^- were formed in the flowing afterglow ion source, and that there was negligible photodetachment into the $Ge(4^1D_2)$ excited state which is energetically accessible at 488 nm, but corresponds to a forbidden transition.

The corresponding data for Sn^- photodetachment are shown in Fig. 2. The observed energy separations of the three largest peaks shown agree with the known[7] fine-structure intervals in $Sn(5^3P_{0,1,2})$ to within 0.5 meV. The electron affinity of Sn is determined to be 1.112 ± 0.004 eV from these data. The much weaker structure in Fig. 2, as well as a similarly weak feature at 0.360-eV electron kinetic energy, is most likely due to SnH^-. As with the Ge^- case no evidence was found for metastable excited Sn^- ions.

The breakdown of Russell-Saunders (*L*-*S*) angular momentum coupling as one moves down the Group IVA column of the periodic table is well known[8] and is most clearly manifested in the progressive decrease in the fine-structure energy ratio $\Delta E(^3P_2 - {}^3P_1)/\Delta E(^3P_1 - {}^3P_0)$, which is 2 for *L*-*S* coupling. The breakdown of *L*-*S* coupling is also seen in the Group-IVA photodetachment transition strengths. The statistical weights for the $^3P_{0,1,2} \leftarrow {}^4S_{3/2}$ tran-

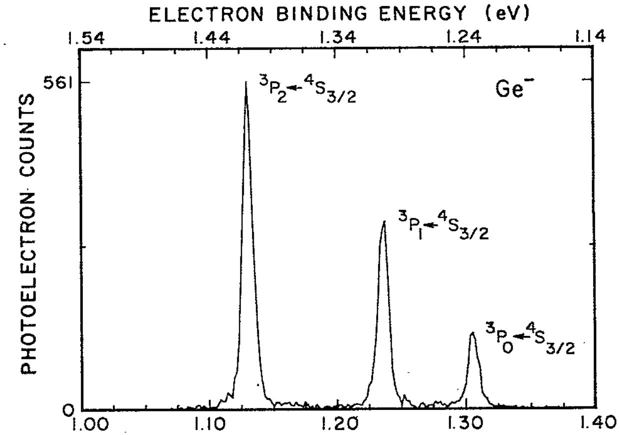

FIG. 1. The photoelectron spectrum of Ge^- obtained with 488-nm (2.540-eV) photons.

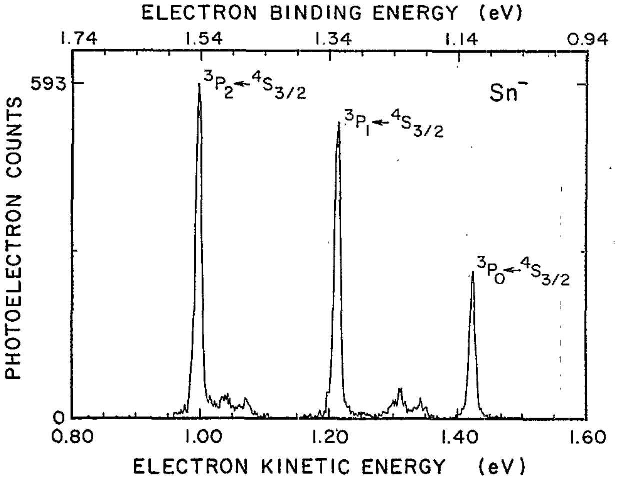

FIG. 2. The photoelectron spectrum of Sn$^-$ obtained with 488-nm (2.540-eV) photons. The weak substructure is due to molecular contamination of the ion beam.

sitions are 1:3:5 in L-S coupling, and these strengths are observed[9] in C$^-$ photodetachment. The relative transition strengths for Si$^-$ have not been determined,[10] but should be quite close to statistical. The present data show that relative transition strengths become more similar as j-j coupling is approached: For Ge$^-$ photodetachment we find 1:2.5:4.1, and for Sn$^-$ we find 1:2.1:2.5. In previous work[11] on Pb$^-$, roughly equal transition strengths were observed. The intensities expected in the j-j coupling limit are not precisely determined, but they will be similar for all transitions. The increasing spin-orbit splitting with atomic number among the Group-IVA elements, and the shift of the $^3P_0$ ground sublevel with respect to the center of gravity of the fine-structure levels due to the breakdown of L-S coupling, may well account[12] for much of the lowering of the electron affinity in going from Si to Pb (from 1.385 to 0.364 eV).[1]

Feldmann *et al.*[2] used a lamp and interference filters in a crossed-beams experiment to measure photodetachment cross sections for Ge$^-$ and Sn$^-$. The electron affinities they determined from photodetachment thresholds were 1.2 ± 0.1 eV for Ge and 1.15 ± 0.15 eV for Sn, which agree quite well with the more accurate values obtained in the present work. In summary, we have used laser photoelectron spectroscopy to determine the electron affinities of Ge (1.233 ± 0.003 eV) and Sn (1.112 ± 0.004 eV). The photodetachment transition strengths at 488 nm provide evidence for the extent of the breakdown of L-S coupling in the ^3P ground states of Ge and Sn.

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