

Photoelectron spectroscopy of As^- , As_2^- , As_3^- , As_4^- , and As_5^-

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The negative ion photoelectron spectra of As^- , As_2^- , As_3^- , As_4^- , and As_5^- have been measured. From these, the electron affinities of As, As_2 , As_3 , As_4 , and As_5 have been determined to be 0.814, 0.739, 1.45, <0.8, and ~ 1.7 eV, respectively. In the case of As_2^- , the following molecular constants were also determined: $r_e(\text{As}_2^-) = 2.239 \text{ \AA}$, $\omega_e(\text{As}_2^-) = 293 \text{ cm}^{-1}$, $\omega_e \chi_e(\text{As}_2^-) = 4.9 \text{ cm}^{-1}$, $D_0(\text{As}_2^-) = 3.89 \text{ eV}$, and $\Delta E[{}^2\Pi_g(3/2) - {}^2\Pi_g(1/2)] = 0.256 \text{ eV}$. In the case of As_3^- , vertical detachment energy (VDE) was measured to be 1.62 eV, and for As_3 , $\Delta E({}^2A_2 - {}^2B_1)$ was determined to be 0.36 eV. For As_4^- , VDE was found to be 1.52 eV. The relatively high stability of As_5^- suggests that it, like P_5^- , may be a candidate for forming cluster-assembled, ionic crystals of stoichiometry, MAs_5 , where M is an alkali metal atom. Similarities with other small cluster anions of Group V elements are also discussed. © 1998 American Institute of Physics. [S0021-9606(98)00748-X]

INTRODUCTION

The compounds of arsenic have a storied history, having been used as pigments since ancient times and having played prominent roles in the early development of both forensics and chemotherapy.¹ Today, they are commonly used to modify the mechanical properties of lead and copper alloys and to eliminate unwanted coloration in glasses. Over the past few decades, elemental arsenic has also begun to find technological uses.²⁻⁹ Elemental arsenic has been shown to have important effects on the molecular-beam epitaxial growth of III-V semiconductors, an example being its role in providing a passivation layer and preventing dopant incorporation during the growth of GaAs on Si surfaces. Numerous studies have also weighed the efficacy of As_2 vs As_4 , with many finding that the use of As_2 yields higher quality films and/or crystals.

Under most sublimation conditions, the dominant species¹⁰ present in arsenic vapor is As_4 . At higher temperatures, however, As_2 dominates, and not surprisingly, at even higher temperatures, only As atoms are seen.¹¹ The abundance of As_3 relative to As_2 and As_4 is suppressed under equilibrium conditions. Both As_2 and As_4 have received considerable attention, both experimentally and theoretically. The arsenic dimer has been studied by electronic emission spectroscopy,¹²⁻¹⁵ photoelectron spectroscopy,¹⁶⁻²⁰ charge-transfer reactions,²¹ and photoionization mass spectrometry.¹¹ Several theoretical calculations have also been performed on the dimer.²²⁻²⁶ The arsenic trimer has been studied via charge-transfer reactions²¹ and photoionization mass spectrometry.¹¹ There have also been some calculations done on this species.^{26,27} In addition, theoretical work on As_2 and As_3 has been reviewed by Balasubramanian.²⁸ The arsenic tetramer has been investigated via photoelectron spectroscopy,^{17-20,29} photoionization mass spectrometry,¹¹ equilibrium studies (with As_2),³⁰ charge-transfer reactions,²¹

Raman spectroscopy,³¹ and gas-phase electron diffraction measurements,³² with the latter finding the structure of As_4 to be tetrahedral. There have also been calculations^{23,25,26,33-35} on As_4 .

The anions of arsenic and its clusters have also been the subject of several studies. Feldmann and co-workers³⁶⁻³⁸ conducted tunable, threshold photodetachment experiments on As^- , finding the electron affinity, EA, of the arsenic atom to be 0.81 ± 0.03 eV. Haefliger and co-workers³⁹ used pulsed photoelectron spectroscopy to measure the energies of the As^- fine structure components, but they did not measure EA(As). Feldmann and co-workers⁴⁰ also conducted tunable, threshold photodetachment spectroscopy on As_2^- , finding the adiabatic electron affinity (EA_a) of As_2 to be 0.1 ± 0.18 eV. Based on appearance potential measurements, Bennett and co-workers⁴¹ reported values for $\text{EA}_a(\text{As}_2)$ and $\text{EA}_a(\text{As}_3)$ of 0.1 ± 0.2 and 0.8 ± 0.4 eV, respectively. Recently, Polak and co-workers⁴² reinterpreted the As_2^- photodetachment threshold data of Feldmann and co-workers⁴⁰ and presented a revised value for $\text{EA}_a(\text{As}_2)$ of 0.70 ± 0.10 eV. Calculations on As_2^- found its bond length increases relative to that of As_2 , and $\text{EA}_a(\text{As}_2)$ to be 0.48 eV.²⁵ Although there have apparently been no calculations on As_3^- , its structure is thought to be linear.⁴³ The literature gives no information on As_4^- . Related work on small cluster anions of other Group V elements has also been reported, the most pertinent being negative-ion photoelectron (photodetachment) spectroscopic studies^{42,44-47} of P_n^- , Sb_n^- , and Bi_n^- .

Here, we report the results of our negative-ion photoelectron spectroscopic study of As^- , As_2^- , As_3^- , As_4^- , and As_5^- . We have been engaged in a search for especially stable clusters (Magic Clusters), and we were motivated to conduct the present study, in part, by reports of unusually stable cluster anions of Group V elements.^{48,49} In particular, the pentamer anions of the Group V elements (except for nitrogen) appear to be quite stable. These anions are predicted by theory to have planar ring structures with pseudoaromatic

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character. Furthermore, the compounds, LiP_5 and NaP_5 have been synthesized in solution,⁵⁰ raising the possibility that they might be able to form ionic crystals. The present study, dealing with the properties of arsenic cluster anions, was part of a larger effort aimed at investigating potential candidates for forming cluster-assembled materials.

EXPERIMENT

Negative-ion photoelectron spectroscopy is conducted by crossing a mass-selected negative ion beam with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The mass selector used in these experiments was a Wein (E×B) filter. The photon source was an argon ion laser, operated intracavity. The electron energy analyzer was a hemispherical instrument, operated with a 28 meV resolution. Our apparatus has been described in detail previously.⁵¹

The negative ion photoelectron spectroscopic technique is a direct approach for determining electron binding energies (EBE), relying on the relationship,

$$h\nu = \text{EBE} + \text{KE}_e, \quad (1)$$

in which $h\nu$ is the photon energy, and KE_e is the measured photoelectron kinetic energy. The photoelectron spectra of $\text{As}_{n=1-4}^-$ were calibrated against the well-known photoelectron spectra^{52,53} of O- and NO-, and were recorded with a photon energy of 2.497 eV. Calibrations for $\text{As}_{n=2-4}^-$ were also confirmed relative to the photoelectron spectrum of As^- . The anions of arsenic and its clusters were generated in a hot, supersonic expansion ion source by heating elemental arsenic to 650–700 K in the argon-filled (~ 3 atm.) stagnation chamber of the source. The resulting arsenic vapor was coexpanded with argon through a 125 μm nozzle orifice. Anions were formed by injection of electrons from a thoriated-iridium filament directly into the expanding jet in the presence of an axial magnetic field. Typically, the filament was biased at -75 V relative to the stagnation chamber, giving an emission current of ~ 10 mA. The stagnation chamber itself was floated at -500 V, i.e., the beam energy.

RESULTS AND INTERPRETATION

As^-

The ground state of As is $4S_{3/2}$, followed by its first excited state, $2D_{3/2,5/2}$. Electronic energy splittings for the arsenic atom are tabulated in the literature.⁵⁴ The ground state of As^- is $3P_{2,1,0}$, with $3P_2$ being the lowest in energy. The photoelectron (photodetachment) spectrum of As^- , recorded with 2.497 eV photons, is presented in Fig. 1. Its assignment is straightforward. The tallest peak in this spectrum is due to the $\text{As}, 4S_{3/2} \leftarrow \text{As}^-, 3P_2$ transition, the origin transition. From the energy of this transition, we determined the $\text{EA}(\text{As})$ to be 0.814 ± 0.008 eV. This is in good agreement with Feldmann's value of 0.81 ± 0.03 eV.^{36,37} The two peaks to lower electron-binding energy, EBE, are assigned as labeled, i.e., $\text{As}, 4S_{3/2} \leftarrow \text{As}^-, 3P_1$ and $\text{As}, 4S_{3/2} \leftarrow \text{As}^-, 3P_0$. We measured the splittings between the fine structure components of the anions's ground state to be 0.127 ± 0.016 eV for $\Delta E(3P_1 - 3P_2)$ and 0.161 ± 0.016 eV for $\Delta E(3P_0$

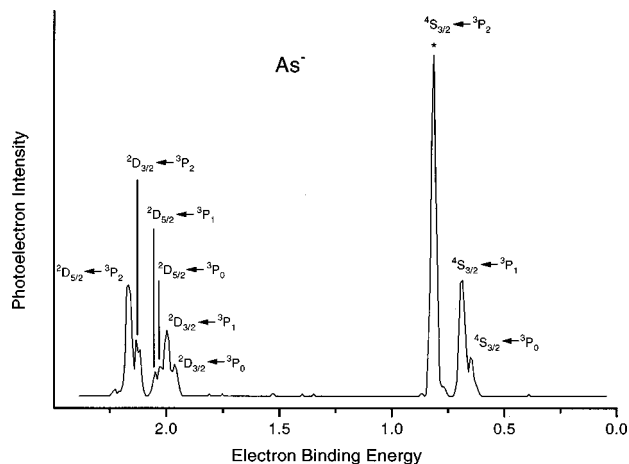


FIG. 1. The assigned photoelectron spectrum of As^- recorded with 2.497 eV photons. (* indicates the origin transition.)

$-3P_2)$. These values are in excellent agreement with those determined previously. Feldmann and co-workers^{36,37} determined $\Delta E(3P_0 - 3P_2)$ to be 0.17 eV. They did not report a value for $\Delta E(3P_1 - 3P_2)$. Haeffler and co-workers³⁹ determined $\Delta E(3P_1 - 3P_2)$ to be 0.125 eV and $\Delta E(3P_0 - 3P_2)$ to be 0.166 eV. The peaks on the high EBE side of the spectrum are due to transitions between the ground state of As^- and the first excited state of the As neutral. They are assigned as labeled, i.e., in order of ascending EBE: $\text{As}, 2D_{3/2} \leftarrow \text{As}^-, 3P_0$; $\text{As}, 2D_{3/2} \leftarrow \text{As}^-, 3P_1$; $\text{As}, 2D_{5/2} \leftarrow \text{As}^-, 3P_0$; $\text{As}, 2D_{5/2} \leftarrow \text{As}^-, 3P_1$; $\text{As}, 2D_{3/2} \leftarrow \text{As}^-, 3P_2$; and $\text{As}, 2D_{5/2} \leftarrow \text{As}^-, 3P_2$.

As_2^-

The electronic ground state of As_2 is $1\Sigma_g^+$, while its first excited state, ~ 1.8 eV higher in energy, is $3\Sigma_u^+$. The ground state of As_2^- is 2Π , and it is split by spin-orbit interactions into $2\Pi_g(1/2)$ and $2\Pi_g(3/2)$, the former being the lower in energy. The photoelectron spectrum of As_2^- , recorded with 2.497 eV photons, is presented in Fig. 2. We attribute the main vibronic progression in this spectrum to the transitions,

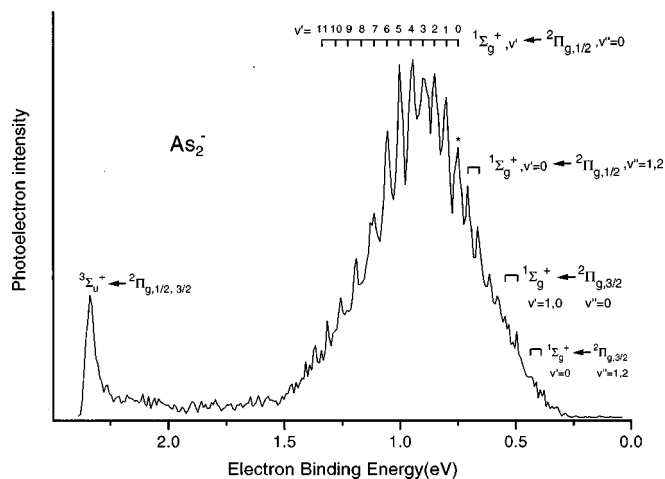


FIG. 2. The assigned photoelectron spectrum of As_2^- recorded with 2.497 eV photons. (* indicates the origin transition.)

$\text{As}_2(X^1\Sigma_g^+, v') \leftarrow \text{As}_2^-(^2\Pi_g(1/2, 3/2), v'')$. The vibrational spacings observed toward the middle and the high EBE side of this spectral profile are relatively evenly spaced and compare well with the 53 meV literature value⁵⁵ for the vibrational frequency of neutral As_2 , while the peak spacings at the low EBE side of the profile are smaller and irregularly spaced. The peak corresponding to the origin transition, $\text{As}_2(X^1\Sigma_g^+, v'=0) \leftarrow \text{As}_2^-(^2\Pi_g(1/2), v''=0)$, was identified based on the observations that the spacing between it and the next higher EBE peak is 51 meV, while the spacing between it and the next lower EBF peak is 42 meV. Given this assignment, we find $EA_a(\text{As}_2)$ to be 0.739 ± 0.008 eV, in agreement with Polak's reinterpretation of Feldmann's data. The lower EBE features in this profile are due to a combination of vibrational and electronic hot bands. The spectral feature at the far left side of Fig. 2 is due to transitions between As_2^- and the $^3\Sigma_u^+$ excited state of As_2 . We see only the edge of this transition, however, the remainder being either beyond our photon energy range or cut off by the transmission function of the electron analyzer.

The energetic relationship between $EA_a(\text{As}_2)$, $EA(\text{As})$, $D_0(\text{As}_2^-)$, and $D_0(\text{As}_2)$ is

$$EA_a(\text{As}_2) - EA(\text{As}) = D_0(\text{As}_2^-) - D_0(\text{As}_2). \quad (2)$$

Having determined $EA_a(\text{As}_2)$ and $EA(\text{As})$ and using the literature value⁵⁵ of 3.96 eV for $D_0(\text{As}_2)$, we computed the value of $D_0(\text{As}_2^-)$ to be 3.89 ± 0.02 eV. Balasubramanian²⁸ estimates the value of $D_0(\text{As}_2)$ to be 3.8 eV, believing the 3.96 eV value obtained from extrapolation to be too large. If this is a better number for $D_0(\text{As}_2)$, then the value of $D_0(\text{As}_2^-)$ would be lowered by 0.16 eV as well. In either case, however, these values imply that the bond strength of As_2^- is weaker than that of As_2 , consistent with bonding arguments based on molecular orbital occupations.

Franck-Condon analysis of the As_2^- photoelectron spectrum corroborated our assignment of the photoelectron spectrum and provided values for several molecular constants. This analysis was conducted using a program developed by Ervin and Lineberger.⁵⁶ It models both anion and neutral electronic potential curves as Morse oscillators. The final fitted spectrum was the result of modeling transitions from two separate anion potential-energy curves (one for each of the spin-orbit components) and combining their intensities. Spectral assignments are indicated on Fig. 2. The input parameters for neutral As_2 [$r_e(\text{As}_2) = 2.102$ Å, $\omega_e(\text{As}_2) = 429.55$ cm^{-1} , and $\omega_e\chi_e(\text{As}_2) = 1.117$ cm^{-1}] were taken from the literature.⁵⁵ Optimization of the fit (see Fig. 3) gave the following molecular constants for the As_2^- anion: $r_e(\text{As}_2^-) = 2.239 \pm 0.010$ Å, $\omega_e(\text{As}_2^-) = 293 \pm 40$ cm^{-1} , $\omega_e\chi_e(\text{As}_2^-) = 4.9$ cm^{-1} , and $\Delta E[^2\Pi_g(3/2) - ^2\Pi_g(1/2)] = 0.256 \pm 0.016$ eV. These values for $r_e(\text{As}_2^-)$ and $\omega_e(\text{As}_2^-)$ are consistent with the expectation that As_2^- should have a weaker bond than As_2 and thus, a longer bond length and a smaller vibrational frequency. Our measurement of $\Delta E[^2\Pi_g(3/2) - ^2\Pi_g(1/2)]$, the spin-orbit splitting in As_2^- , is the first report of this quantity, and as expected, its value lies between that for P_2^- (0.020 eV)⁴⁵ and Sb_2^- (0.305 eV).⁴²

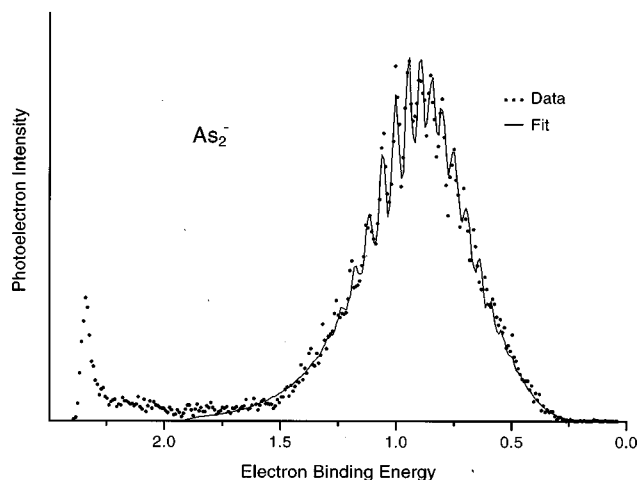


FIG. 3. A comparison of the experimental and the modeled photoelectron spectrum of As_2^- .

[The spin-orbit splitting in Bi_2^- has been calculated to be ~ 1 eV.⁵⁷] The optimized fit also gave a temperature of 775 K.

As_3^-

Calculations predict the ground state of As_3 to have a D_{3h} equilateral structure. Jahn-Teller distortions lift this degeneracy, yielding two C_{2v} structures, the X^2A_2 and 2B_1 states.²⁸ As mentioned above, the structure of As_3^- is probably linear.⁴³ The photoelectron spectrum of As_3^- , recorded with 2.497 eV photons, is presented in Fig. 4(c). Two major bands appear in this spectrum, and they are labeled as A and B. We assign band A as being due to the transition between the anion's ground state and the 2A_2 ground state of As_3 and band B as being due to the transition between the anion's ground state and the 2B_1 state of As_3 . The EBE of the peak maximum in band A is the vertical detachment energy, VDE, of As_3^- , and it is 1.62 ± 0.03 eV. If one assumes, following Polak and co-workers,⁴² that the origin will be shifted from the center of band A towards lower EBE by the same fraction of the bandwidth that the vibrationally-resolved and assigned As_2^- spectrum was shifted, then $EA_a(\text{As}_3) = 1.45 \pm 0.03$ eV. (The onset of a signal which is detectable above the baseline occurs at an EBE of ~ 1 eV.) The splitting between bands A and B is dominated by Jahn-Teller effects in As_3 , and we measure it to be 0.36 eV. The fact that bands A and B appear to have similar widths suggests that similar magnitudes of anion-to-neutral geometry changes are probably involved in both transitions. The photoelectron spectrum of As_3^- is qualitatively similar to those of other Group V trimer anions.^{42,44-47} Bands A and B, with band A being more intense than band B, are seen in the photoelectron spectra of P_3^- , Sb_3^- , and Bi_3^- .

As_4^-

The arsenic tetramer, As_4 , has a tetrahedral structure, and its ground state is 1A_1 , while the ground state of As_4^- is probably 2T_1 . The photoelectron spectrum of As_4^- , recorded with 2.497 eV photons, is presented in Fig. 4(d). The spectrum is dominated by a broad band having a VDE of 1.52

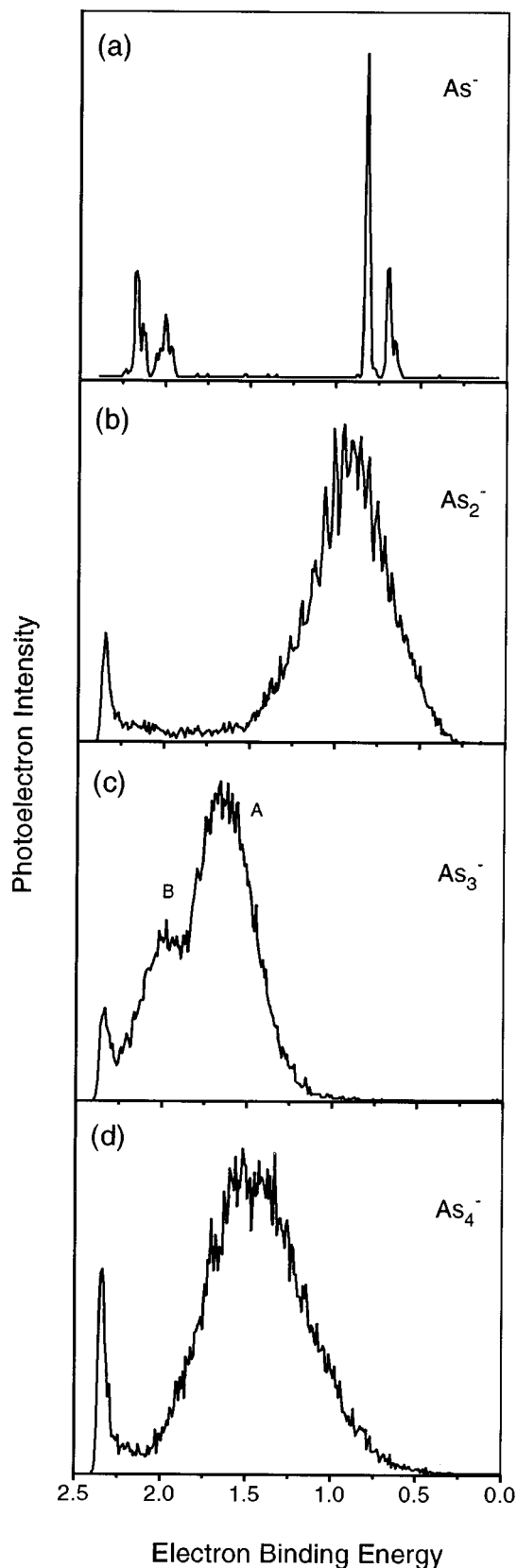


FIG. 4. A comparison of the photoelectron spectra of (a) As^- , (b) As_2^- , (c) As_3^- , and (d) As_4^- . All of these were recorded with 2.497 eV photons.

± 0.03 eV. We assign this band as arising from the transitions between the ground state of As_4^- and the ground state of As_4 . The large width of this band is indicative of a large

geometry difference between the equilibrium structures of the anion's ground state and the neutral's ground state. This, and the lack of assignable structure in this band, make the identification of the origin difficult. The onset of photoelectron counts detectable above the noise occurs at an EBE of 0.44 eV. This may not be the origin, however, since hot bands are often responsible for signals at the low EBE end of photoelectron spectra. It is even possible that the structural difference between the anion and its corresponding neutral is so great that the origin transition is not visible in this spectrum. Given these uncertainties, we prefer to set an upper limit for $\text{EA}_a(\text{As}_4)$ of ~ 0.8 eV. We also see the edge of another feature at the high EBE end of the spectrum. This is likely to be due to transitions between the anion's ground state and the first excited state of As_4^- . Last, we note that the profiles of the photoelectron spectra of Sb_4^- , Bi_4^- , and especially P_4^- qualitatively resemble that of As_4^- .

As_5^-

We also have measured a low-count photoelectron spectrum of As_5^- , again with 2.497 eV photons. We observed one, and possibly two, bands at the high EBE end of the spectrum. The onset of a detectable signal began at an EBE of ~ 1.5 eV, with the photoelectron intensity rising substantially toward higher EBE. We estimate $\text{EA}_a(\text{As}_5)$ to be ~ 1.7 eV or higher. The enhanced stability of As_5^- suggests that, like P_5^- , it may well be a candidate for forming cluster-assembled, ionic crystals of stoichiometry, MAAs_5 , where M is an alkali metal atom.

DISCUSSION

Figure 4 compares the photoelectron spectra of As^- , As_2^- , As_3^- , and As_4^- . From these and our crude spectrum of As_5^- , we have determined the electron affinities of As, As_2 , As_3 , As_4 , and As_5 to be 0.814, 0.739, 1.45, < 0.8 , and ~ 1.7 eV, respectively. This series exhibits an alternating electron affinity vs size trend. While the electron affinities of As and As_2 are comparable, the electron affinity of As_3 increases relative to that of As_2 , the electron affinity of As_4 decreases relative to that of As_3 , and the electron affinity of As_5 increases dramatically relative to that of As_4 . This same alternating electron-affinity trend is also seen in the like-size clusters of phosphorus, antimony, and bismuth.^{42,44-47} With the addition of the present results on arsenic cluster anions, all of the small cluster anions of the Group V elements (except for nitrogen, where N^- and N_2^- are unstable and only N_3^- has been investigated⁵⁸) have now been studied by negative ion photoelectron spectroscopy.

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