Photoelectron spectroscopy of small antimony cluster anions: Sb\textsuperscript{−}, Sb\textsubscript{2}\textsuperscript{−}, Sb\textsubscript{3}\textsuperscript{−}, and Sb\textsubscript{4}\textsuperscript{−}

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We report the 351 nm photoelectron spectra of Sb\textsuperscript{−}, Sb\textsubscript{2}\textsuperscript{−}, Sb\textsubscript{3}\textsuperscript{−}, and Sb\textsubscript{4}\textsuperscript{−}. The electron affinity of atomic Sb is measured to be 1.046(5) eV. The Sb\textsubscript{2}\textsuperscript{−} photoelectron spectrum displays rich vibrational and electronic structure. Low-lying electronically excited states are observed for both the anion and the neutral. Several features in both the 351 and 364 nm photoelectron spectra of Sb\textsubscript{2}\textsuperscript{−} cannot be explained as Franck-Condon processes, indicating that we are accessing autodetaching resonances of the negative ion at these wavelengths. The adiabatic electron affinity of Sb\textsubscript{2} is determined to be 1.282(8) eV. For the photoelectron spectra of Sb\textsubscript{3}\textsuperscript{−} and Sb\textsubscript{4}\textsuperscript{−}, the observed electronic structure is explained in terms of recently reported \textit{ab initio} calculations. The adiabatic electron affinity of Sb\textsubscript{3} is estimated to be 1.85(3) eV, and an upper bound on the electron affinity of Sb\textsubscript{4} is reported, EA(Sb\textsubscript{4}) < 1.00(10) eV. The vertical detachment energies of Sb\textsubscript{3}\textsuperscript{−} and Sb\textsubscript{4}\textsuperscript{−} to the neutral ground states are determined to be 1.90(2) and 1.57(5) eV, respectively. We report photoelectron angular distributions for all the observed spectra, and find that the autodetaching resonance causes unusual angular distributions for Sb\textsubscript{2}\textsuperscript{−} photodetachment. Finally, electron affinity trends for group V atoms, dimers, and small clusters are discussed in light of the present study.

I. INTRODUCTION

The structural and electronic properties of small metal clusters have generated considerable interest in recent years.\textsuperscript{1} Not only do small metal clusters provide a basis for understanding the transition from molecular to bulk behavior in metals, but they also represent a unique class of chemical compounds which, despite much recent progress, remains largely uncharacterized. Negative ion photoelectron spectroscopy has proven to be an especially powerful technique for probing basic properties of small clusters. Recently, we have applied this technique to main group dimers,\textsuperscript{3} Sn\textsubscript{2}, Pb\textsubscript{2}, and SnPb\textsuperscript{−}. In general, the electronic structure of atomic Sb is well characterized.6 The spectroscopic investigation of the electronic structure of Sb\textsubscript{3} has been published by Balasubramanian.6 The spectroscopic investigations of interest for our study are those which have probed the low-lying electronic states accessible with our photoelectron spectrometer (<17 000 cm\textsuperscript{−1} above the ground state of Sb\textsubscript{2}). Of these, only the \textit{X} \textit{1}Σ\textsubscript{g}\textsuperscript{+} (0\textsubscript{Π}\textsuperscript{+}) (Ref. 7) and the \textit{A} \textit{3}Δ\textsubscript{g} (1\textsubscript{Π}) (Ref. 8) states have been characterized by experiments. Balasubramanian and Li9 have performed high-level \textit{ab initio} calculations on 44 electronic states below 44 000 cm\textsuperscript{−1}, including relativistic configuration-interaction (RCI) treatments for many of these states. These previous experimental and theoretical efforts will be discussed in relation to the photoelectron spectrum.

Antimony trimer has not been observed spectroscopically. Using matrix-isolation spectroscopy, Sontag and Weber\textsuperscript{10} tentatively assigned a resonance Raman feature to the trimer; however, in a subsequent study\textsuperscript{11} the feature was reassigned to Sb\textsubscript{4}. Balasubramanian, Sumathi, and Dai\textsuperscript{12} have performed quantum-chemical calculations on Sb\textsubscript{4} to estimate the energies of the five lowest electronic states corresponding to a triangular structure.

Antimony tetramer is the primary component of the antimony vapor\textsuperscript{13} and has been the subject of several matrix-isolation spectroscopic investigations. Sontag and Weber\textsuperscript{10} and Bondybey, Schwartz, and Griffiths\textsuperscript{14} have used Raman spectroscopy to determine fundamental vibrational frequencies; the results were consistent with a tetrahedral geometry. Recently, Zhang and Balasubramanian\textsuperscript{15} have performed high-level quantum-chemical calculations on the lowest six electronic states of tetrahedral Sb\textsubscript{4}.

Wang and co-workers have reported the HeI (584 Å) photoelectron spectra of both antimony dimer\textsuperscript{16} and tetramer,\textsuperscript{17} probing the electronic structures of the respective cations. The tetramer photoelectron spectrum provides some interesting comparisons to our Sb\textsubscript{4}\textsuperscript{−} spectrum.
thermochemistry of small antimony clusters has been of some interest as well. Kordis and Gingerich have used Knudsen effusion mass spectrometry to determine heats of atomization for Sb$_2$-4. Combining these values with electron affinities leads to the determination of thermodynamic stabilities for the respective anions.

In the present study we report the 351 nm photoelectron spectra of Sb$_7$-4. To our knowledge, there have been no previous spectroscopic studies of the negative ions, except for Sb$_{-}$. First, we present a brief description of the experimental methods. Next, the individual photoelectron spectra are presented and analyzed, and the results are compared to previous spectroscopy and quantum-chemical calculations. Then the photoelectron angular distributions measured for all four species are presented and discussed. Finally, the trends observed for the electron affinities of small group V clusters are discussed.

II. EXPERIMENT

The cold cathode discharge metal cluster source and the photoelectron spectrometer have been described previously in detail; only the basic features are summarized here. Ions are formed in an antimony cathode discharge source. The cathode consists of an approximately 8 cm long piece of a 1 cm diameter antimony rod (Aesar, 99.9% purity), and is maintained at $-2$ to $-4$ kV with respect to ground. In this manner, a discharge is struck between the cathode and the chamber walls. The primary carrier gas is helium [500 mTorr, 4 standard liters per minute (SLPM)], seeded with approximately 10% argon to promote sputtering. The ions are allowed to equilibrate with the carrier gas in a 0.25 m long flow tube, at the end of which the negative ions are extracted through a 0.5 mm pinhole into a differentially pumped region. Typical ion currents, measured at a Faraday cup at the end of the beamline, are 5 pA of Sb$^-$, 45 pA of Sb$_2^-$, 125 pA of Sb$_3^-$, and 450 pA of Sb$_4^-$. Following extraction, the ions are mass selected by a Wien filter, and the mass-selected ions are crossed by 351 or 364 nm laser light. Electrons ejected perpendicular to the laser-beam–ion-beam plane are collected and energy analyzed in a hemispherical analyzer with 8–10 meV resolution. The absolute energy scale is calibrated against the precisely known electron affinity of oxygen, and the relative energy scale is calibrated against the energy-level spacings of tungsten and antimony atoms, as measured in the photoelectron spectra of the atomic anions. The absolute position of a well-resolved peak can be measured to an accuracy of $\pm 5$ meV. The photoelectron spectra are expressed in terms of electron kinetic energy (eKE) or electron binding energy (eBE = h\nu - eKE). The electron binding energy of a transition does not change with photon energy.

Because the electron collection angle is fixed, the angular dependence of the photodetachment cross section can be studied by rotating the laser polarization with a half-wave plate. In the electric dipole approximation, the angular dependence of a photodetachment cross section is given by

$$d\sigma/d\Omega = (\sigma_0/4\pi) \left[ 1 + \left( \beta/2 \right) (3 \cos^2 \theta - 1) \right],$$

where $\theta$ is the angle between the laser polarization vector and the direction of electron ejection, and $\beta$ is the asymmetry parameter $(-1 < \beta < 2)$. Generally, the laser polarization is set at the "magic angle" ($54.7^\circ$ where $3 \cos^2 \theta - 1 = 0$) such that the spectral intensities are proportional to the total photodetachment cross section. In order to measure $\beta$ for each transition the photoelectron spectra are measured at $\theta = 0^\circ$ and $\theta = 90^\circ$. To determine $\beta$ accurately for individual peaks, the angular dependence of the largest peaks in the spectra are measured in $10^\circ$ intervals, and the observed intensities are least-squares fit to Eq. (1). These values of $\beta$ can then be used to scale the $\theta = 0^\circ$ and $\theta = 90^\circ$ spectra with respect to one another.

III. RESULTS, ANALYSIS, AND DISCUSSION

A. Sb$^-$

The 351 nm photoelectron spectrum of Sb$^-$ is shown in Fig. 1. The spectrum corresponds to transitions from the negative-ion ground state to various electronic states of the neutral atom, which are assigned in Table I according to well-known energy levels of the neutral. No evidence of hot bands resulting from electronic excitation of the anion was observed. From the electron binding energy of the ground–ground state transition (transition a in Fig. 1), the

![FIG. 1. The 351 nm photoelectron spectrum of Sb$^-$. From the position of peak a, we determine an electron affinity for atomic antimony of 1.046(5) eV.](image)

### TABLE I. Assignment of the 351 nm photoelectron spectrum of Sb$^-$ including angular distributions.

<table>
<thead>
<tr>
<th>Label</th>
<th>Assignment</th>
<th>eKE (eV)</th>
<th>eBE (eV)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$^4S_{1/2} \rightarrow ^2P_1$</td>
<td>2.485</td>
<td>1.046</td>
<td>0.52</td>
</tr>
<tr>
<td>b</td>
<td>$^2D_{3/2} \rightarrow ^2P_1$</td>
<td>1.430</td>
<td>2.101</td>
<td>-0.38</td>
</tr>
<tr>
<td>c</td>
<td>$^2D_{3/2} \rightarrow ^2P_1$</td>
<td>1.263</td>
<td>2.268</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

*The spacings in the Sb$^-$ spectrum, which correspond to accurately known atomic energy levels in Sb, were used to calibrate the relative energy scale of the spectrometer. Therefore, the values in this table should not be construed as a measurement of Sb atomic energies.*
state of the negative ion, through which additional levels of electronic bands emanating from the Sb\textsuperscript{−} ground state are observed: band a \([\Sigma_g^+ - \Pi_g(1/2_g)]\), band c \([\Sigma_g^+ - \Pi_g(1/2_g)]\), and band d \([\Delta_u - \Pi_u(1/2_u)]\). In addition an electronic hot band is observed, band a’ \([\Sigma_g^+ - \Pi_g(3/2_g)]\), as well as weak transitions (b) to highly vibrationally excited levels of the \(1\Sigma_g^+\) Sb\textsubscript{2} ground state.

The measurement is in good agreement with the previously measured \(1.07 \pm 0.05\) eV, but with a tenfold increase in precision.

**B. Sb\textsubscript{2}**

1. **Results and Franck–Condon analysis**

Of the four species examined in the present study, the most extensive new information is obtained for antimony dimer. Figure 2 displays an overview of the 351 nm spectrum, showing three prominent electronic transitions (a, c, and d). Based on the established electronic structure of Sb\textsubscript{2} \textsuperscript{−} and on \textit{ab initio} calculations of Sb\textsubscript{2}, a, c, and d can be assigned as transitions from the anion ground state \([\Sigma_g^+(1/2_g)]\) (Ref. 24) to the \(1\Sigma_g^+, 3\Sigma_g^+,\) and \(3\Delta_u\) states of the neutral. In addition, an electronic hot band is observed (a’), as well as weak continuous vibrational structure (b).

The most unusual feature of the spectrum is the weak continuous vibrational structure that extends almost 1 eV, from the end of band a to the beginning of band c. The peak centers have irregular spacings ranging from 220 to 270 cm\textsuperscript{−1}, and the line shapes are similarly irregular. Although these spacings vary, there is a general tendency toward smaller spacing with increasing electron binding energy, and the highest observed spacing (270 cm\textsuperscript{−1}) is the vibrational frequency observed in band a. Based on these observations we assign feature b to transitions to highly excited vibrational states of the electronic ground state \((1\Sigma_g^+\)) of Sb\textsubscript{2}.

Normally, we expect vibrational transition intensities in photoelectron spectra to be governed by the Franck–Condon principle; however, feature b cannot be explained in these terms. We suggest that the deviation from Franck–Condon intensities is caused by an accidental resonance, where the 351 nm (3.531 eV) light accesses a short-lived state of the negative ion, through which additional levels of the neutral molecule can be accessed. To test this hypothesis we changed the photodetachment wavelength to 364 nm (3.408 eV). Figure 3 displays the 364 nm photoelectron spectrum. Feature b is enhanced, and the intensities and shapes of features c and d have changed completely. For direct photodetachment well above threshold (\(> 0.5\) eV), a small change in photon energy should merely shift the electron kinetic energy scale of the spectrum, with very little change in relative intensities. The observed change in intensities is indicative of contributions from resonant photodetachment, and the presence of non–Franck–Condon features at both wavelengths suggests that the excited negative-ion state is very broad. Although the resonance occurs at both wavelengths, the effects are greatly enhanced at 364 nm. Similar behavior has been observed for Cr\textsubscript{2},\textsuperscript{25} phenoxide \((\text{C}_6\text{H}_5\text{O})\),\textsuperscript{26} S\textsubscript{2} \textsuperscript{−},\textsuperscript{27} and propadienyli-dene \((\text{C}_3\text{H}_4\text{O})\).\textsuperscript{27}

The irregular spacings and line shapes observed in feature b are most likely due to the intensities of transitions from different negative-ion vibrational states changing relative to one another throughout the progression. The approximate amount of vibrational energy in any neutral state can be determined by the difference in electron binding energy between a given peak and the origin peak in band a. Using our vibrational origin assignment for band a (described subsequently), we count peaks to determine an assignment of \(v = 33\) for the peak at 2.299 eV electron binding energy, with a total vibrational energy (above zero point) of 1.017(6) eV \((8202(50)\) cm\textsuperscript{−1}). The vibrational constants of Gerber and Kuscher\textsuperscript{24} for the ground state of Sb\textsubscript{2}, which include a second-order anharmonicity, predict a vibrational energy of 8222 cm\textsuperscript{−1} above zero point for \(v = 33\). This provides strong support for our assignment of feature b to vibrationally excited states of the Sb\textsubscript{2} electronic ground state.

Interestingly, the only features that are not strongly affected by the change in wavelength are bands a and a’. The simplest explanation for this is that the short-lived
negative ion state accessed by the resonance is weakly bound (has a large bond length), and autodetaches only to states that sample large internuclear separation. The highest occupied molecular orbitals of $\text{Sb}_2^-$ arise from combinations of atomic $5p$ orbitals, resulting in the electronic configuration $\alpha^2 \gamma^2 \pi^4 \eta^2$. The transitions of bands $a$ and $a'$ involve detachment from a $\pi_u$ antibonding orbital to obtain a $^1\Sigma_u^+$ state with a smaller bond length, while bands $c$ and $d$ result from detachment from a $\pi_u$ bonding orbital resulting in the larger bond length $^1\Sigma_u^+$ and $^3\Delta_u$ states. It appears that the resonant state autodetaches preferentially to the larger bond-length electronic states and to highly vibrationally excited states of the smaller bond-length electronic state—in other words, to vibrational states which sample larger $r$.

Because the 351 nm spectrum appears to be less affected by the resonance than the 364 nm spectrum, we will use it for the Franck-Condon analysis of bands $a'$, $a$, $c$, and $d$. Since bands $a$ and $a'$ appear to be only slightly affected by the resonance, molecular constants obtained from Franck-Condon simulation of these bands should be reliable. We will also show that bands $c$ and $d$ in the 351 nm spectrum can be modeled as Franck-Condon progressions, each involving transitions to two spin–orbit components of a neutral electronic state, and yielding reasonable molecular constants. However, it is very likely that the profiles of bands $c$ and $d$ are severely affected by the resonance. Therefore, the Franck-Condon simulations of these bands should be viewed only as plausible models of the observed intensities, rather than being definitive.

One concern in the analysis is that the photoelectron spectra were obtained using a mixture of naturally occurring isotopes. Antimony has two naturally occurring isotopes: $^{121}\text{Sb}$ (57.3%) and $^{123}\text{Sb}$ (42.7%). The ensuing Franck-Condon analysis was performed using the reduced mass for the $^{121}\text{Sb}^-^{123}\text{Sb}$ isotopomer. Contributions to the spectrum from the other isotopomers are not expected to affect the derived constants within the experimental precision. One might expect the high $v'$ end of a vibrational progression to be slightly broadened by the presence of three isotopomers. However, even at $v'=6$ of the $\text{Sb}_2$ ground state the range of vibrational energies is only 11 cm$^{-1}$ (1.4 meV), which, given the instrumental resolution of 8–10 meV, cannot be distinguished from the broadening caused by vibrational congestion due to hot bands [see Fig. 4(a)].

The Franck-Condon analysis procedure has been described in some detail.\textsuperscript{20} The anion and neutral electronic states are modeled as Morse oscillators, and Franck-Condon factors are determined by numerical integration of the overlap of the Morse oscillator wave functions. The parameters which can be adjusted in the analysis are the bond-length change, anion and neutral vibrational frequencies and anharmonicities, position and intensity of the origin transition, a Gaussian instrumental linewidth function, and the anion vibrational temperature. The fitting procedure consists of both visual and least-squares optimization of the simulated spectrum to the experimental data. In this manner, the frequency and intensity information contained in the spectrum are simultaneously used to extract molecular constants. Error bars are determined empirically by varying parameters until the quality of the fit degrades significantly (as determined visually); care is taken to ensure that the degradation cannot be offset by adjusting other parameters. Because of the small rotational constant of $\text{Sb}_2$, the rotational contribution to the line shape is calculated to be less than 1 meV and can be neglected.

FIG. 4. Franck-Condon simulations of the $\text{Sb}_2^-$ electronic bands using the molecular constants in Table II. Data are represented by points, the simulated spectra are drawn as solid lines, and individual vibrational transitions are plotted as sticks. Thick sticks represent transitions from $v'=0$; the remaining structure is due to vibrational hot bands. Arrows indicate vibrationless origins.
Band a' was assigned as a transition from the anion ground state [2Σ⁺(1/2)\_e] to the neutral ground state [2Σ⁺(0⁺)\_e], based on its having the lowest binding energy of the three strong bands, and on its vibrational spacing of 270(10) cm\(^{-1}\) being in agreement with previous measurements\(^7\) of the ground vibrational frequency of Sb\(_2\). The Franck–Condon analysis of this band was carried out by fixing the neutral state constants at literature values\(^8\), and allowing the anion constants and vibrational temperature to vary. To determine the position of the vibrationless origin, several assignments were attempted; only one assignment yielded a suitable fit. The resulting vibrational temperature was 420(10) K, consistent with previous values measured from our ion source. The adiabatic electron affinity was determined to be 1.282±0.008 eV, the binding energy of the origin peak, labeled with an arrow in Fig. 4(a). The finding that the bond length decreased in going from the anion to the neutral arose from the fit; attempts to simulate the spectrum with a bond-length increase were unsuccessful. The anion constants resulting from the analysis are shown in Table II; the simulated spectrum is illustrated in Fig. 4(a). Table II also contains all of the constants obtained from the Franck–Condon fits described below.

Band a' was fit assuming the electronic hot-band assignment, 1Σ⁺(0⁺)\_e \(\rightarrow\) 2Σ⁺(3/2)\_e. The neutral constants were fixed at the values from high-resolution spectroscopy,\(^7\) and the anion constants were allowed to vary. Based on the vibrational temperature determined in the previous fit, only one origin choice was feasible.

The fit of band a using the accurately known ground-state neutral constants provided the key to the remainder of the analysis. For the fits of bands c and d, the anion molecular constants and vibrational temperature could be fixed. Bands c and d presented additional difficulty because of the presence of multiple spin–orbit components with overlapping vibrational progressions. Band c is assigned to the 3Σ⁺\(_u\) state with 0\(^-\) and 1\(_v\) components, and band d is assigned to the 3Σ\(_u\) state which has 1\(_u\), 2\(_u\), and 3\(_u\) components.

The simulation of band c is shown in Fig. 4(b). First, the high electron kinetic-energy tail of the spectrum was fit as one electronic band; only one vibrational origin was possible given the vibrational temperature of 420 K. The simulation of that electronic band over the entire region was then subtracted from the spectrum, leaving one electronic band behind which could be treated in a similar manner. The two fits were summed and simultaneously fit for all of the data. This procedure was repeated for many combinations of origin assignments; only the assignment shown in Fig. 4(b) yielded a satisfactory fit.

To fit band d, we used molecular constants for the 3Δ\(_u\)(1\(_u\)) state which have been determined previously.\(^8\) Using our Sb\(_2\) electron affinity of 1.282 eV in combination with the 3Δ\(_u\)(1\(_u\)) term energy of 14.991 cm\(^{-1}\), the origin for this state was determined to lie at an electron binding energy of 3.141 eV (eKE=0.391 eV at 351 nm). This origin location was used along with the known neutral state vibrational frequency and an estimated bond length to generate a simulation which could then be subtracted. Although we expected the remaining spectrum to result from transitions to two spin–orbit components of the neutral, it could be simulated as a single electronic transition. An origin was easily assigned, given the fixed vibrational temperature (420 K), and by assuming that the geometry of the neutral state was similar (within 0.02 Å) to that of the 1\(_u\) state. For the final simulations [Fig. 4(c)] the two electronic bands were simultaneously fitted, and the neutral state constants for both electronic bands were allowed to vary.

### Table II. Results of Franck–Condon analysis of the 351 nm photoelectron spectrum of Sb\(_2\)^−

<table>
<thead>
<tr>
<th>State</th>
<th>Bands involving this state(^a)</th>
<th>(T_0) (cm(^{-1}))(^b)</th>
<th>(T_0) (cm(^{-1}))(^c)</th>
<th>(\omega_{v_0}) (cm(^{-1}))</th>
<th>(\omega_{v_0}) (cm(^{-1}))</th>
<th>(T_0) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb(_2)^−</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Σ⁺(1/2)_e</td>
<td>a, b, c, d</td>
<td>0</td>
<td>-10 340 (60)</td>
<td>242 (10) 1.2</td>
<td>2.573 (10)</td>
<td></td>
</tr>
<tr>
<td>2Σ⁺(3/2)_e</td>
<td>a'</td>
<td>2460 (40)</td>
<td>236 (10) 0.66</td>
<td>2.571 (10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X^+) 2\Sigma_e</td>
<td>a', a, b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Σ_e(1_u)</td>
<td>c</td>
<td>9 420 (60)</td>
<td>205 (10) 0.95</td>
<td>2.694 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2Σ_e(0_u)</td>
<td>c</td>
<td>10 480 (60)</td>
<td>187 (10) 0.44</td>
<td>2.701 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3\Sigma_a(1_u)</td>
<td>d</td>
<td>13 830 (80)</td>
<td>271 (10) 0.5</td>
<td>2.765 (20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3\Delta_a(1_u)</td>
<td>d</td>
<td>14 970 (80)</td>
<td>215 (10) 0.5</td>
<td>2.654 (20)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Bands in photoelectron spectrum (see Fig. 2) in which these states appear as a lower state (anion state) or an upper state (neutral state).

\(^b\) Referenced to the Sb\(_2\) ground state.

\(^c\) Referenced to the Sb\(_2\) ground state.

\(^d\) Anharmonicity is not well determined in the fit to the spectrum; the values in parentheses were used to obtain the optimized simulations shown in the figures.

\(^e\) Fixed at value from Ref. 7.

\(^f\) Origin assignment based entirely on term energy from Ref. 8.
Approximate potential-energy curves for the low-lying electronic states of Sb$_2$ and Sb$^-$ are shown in Fig. 5. Table III shows molecular constants for these states, obtained from this work, previous experiments, and predicted by ab initio methods. Because the photoelectron transitions to the two excited states of Sb$_2$ are affected by a resonance, those values which rely on intensity measurements (origin assignments and geometry displacements) may not be accurate. Therefore, the term energies and bond lengths obtained for these bands should be regarded as approximate; however, the vibrational frequencies for these states are determined from line spacings and should be reliable.

The vibrational frequencies, spin–orbit splitting, and geometries determined for Sb$^-$ are the first experimental determinations of any molecular constant of this anion. The lowered vibrational frequency and increased bond length observed for the anion (compared to the neutral) are consistent with the additional electron residing in an antibonding orbital. The spin–orbit splitting of this $^2\Sigma^+$ state (2460 cm$^{-1}$) is similar to that of the $^3\Sigma^+$ ground state of SbO (2272 cm$^{-1}$), indicating that it is a typical value for an antimony centered unpaired electron. Our ordering of the $^2\Pi$ spin–orbit components is simply based on Hund’s rules.

Most of the Sb$_2$ neutral states accessed in the photoelectron spectrum have not been examined previously. For the X and A states, the vibrational frequencies measured in the spectrum are in excellent agreement with the previous experiments. Our analysis employed Gerber and Kuscher’s rovibrational constants for the X state. Gerber and Kuscher demonstrate that the value of $r_{eX}$ reported by Sfeila et al. (2.3415 Å) is in error by -0.15 Å. In a recent review, Balasubramanian compared his ab initio $r_e$ value to the $r_{eX}$ value of Sfeila et al. and found a 0.25 Å difference between theory and experiment; the comparison of the ab initio value to the accurate Gerber and Kuscher value of $r_e$ is much better (Table III). Our analysis also employed Almy and Schultz’s measurement of the A–X band of Sb$_2$ at 14 991 cm$^{-1}$, which was later assigned to the $^3\Delta_u$($^1_u$) state by Balasubramanian and Li. The photoelectron spectrum further confirms this assignment as follows. Based on the ordering of states in both As$_2$
and Bi₂ and on ab initio calculations of Sb₂, we expect the order of the first three electronic states of Sb₂ to be $^3\Sigma^+$, $^3\Sigma^-$, and $^3\Delta_u$. Because the 14 991 cm⁻¹ term energy lies within band d, the second excited electronic state we observe, it is assigned to $^3\Delta_u$, and optical selection rules require that it correspond to the $^1\Sigma_u^-$ component.

The ordering we use for the $\Omega$ components of the $^3\Sigma^+$ and $^3\Delta_u$ states is based on the ordering in the ab initio calculations. The transition to the $^3\Delta_u$ state can be accounted for as a transition to only two states, where the additional state is lower in energy than the $^1\Sigma_u^-$ state and is assigned as $^2\Delta_u$. A likely explanation for the absence of the $^3\Delta_u$ transition, suggested by ab initio calculations (see Table III), is that the splitting between the $^1\Sigma_u^-$ and $^3\Delta_u$ states is very small and not resolved here.

Balasubramanian and Li⁹ have carried out extensive calculations on the electronic structure of Sb₃, calculating energies, vibrational frequencies, and bond lengths for 33 electronic states. All of the states observed in this spectrum have been treated at the CASSCF-MRSDCI-RCI [complete-active-space self-consistent-field, multireference singles and doubles configuration-interaction (CI), relativistic CI] level and the results are shown in Table III. The calculations underestimate the term energies of the $^3\Sigma^+_u$ state and overestimate the $^3\Delta_u$ energies by roughly 5%–15%. The biggest discrepancy lies in the splittings between $\Omega$ components. Our $^3\Sigma^+_u$ ($^1\Sigma_u^-$ and $^3\Sigma^-_u$) splittings are a factor of 12 larger than those calculated and our $^3\Delta_u$ ($^1\Sigma_u^-$ and $^2\Delta_u$) splittings are more than a factor of 3 larger. One should recall that our measurements of these splittings may not be entirely reliable due to effects of the resonance on relative intensities. For the $^3\Sigma^+_u$ transition, it is possible that one or both of the vibrational progressions are extended by the resonance resulting in an apparently large splitting. However, for the $^3\Delta_u$ state, previous experiments fix the origin for the $^1\Sigma_u^-$ state. We observe transitions to a state much lower in energy than the $^1\Sigma_u^-$ state, so we know that this state must exist and that the splittings are greatly underestimated by the calculations. The calculations perform superbly in determining the bond-length changes as a function of the electronic state, although the absolute bond length is consistently about 0.1 Å too large. The vibrational frequencies are only about 10–20 cm⁻¹ too low.

To summarize, Table III presents the current state of knowledge concerning the lowest 2 eV of the electronic structure of Sb₃, much of which has been determined in the present study. The first molecular constants determined for Sb₃ are presented as well.

C. Sb₃⁻ and Sb₄⁻ photoelectron spectra

Figures 6 and 7 illustrate the 351 nm photoelectron spectra of Sb₃⁻ and Sb₄⁻. The features labeled in these spectra are catalogued in Table IV. Both spectra contain broad electronic transitions which are not vibrationally resolved. In both cases, state-of-the-art ab initio calculations were essential to the interpretation of the observed electronic structure. In addition, the Jahn–Teller effect plays an important role in the electronic structure of both the $D_{3h}$ structure of Sb₃⁻, much of which has been determined in the present study. The first molecular constants determined for Sb₃⁻ (Ref. 12) of the electronic structure of equilateral triangular Sb₃. From feature a, the adiabatic electron affinity of Sb₃⁻ is estimated to be 1.85(3) eV.

FIG. 6. The 351 nm photoelectron spectrum of Sb₃⁻. Three distinct neutral electronic states are observed (features a, b, and d), which are consistent with ab initio calculations (Ref. 12) of the electronic structure of equilateral triangular Sb₃. From feature a, the adiabatic electron affinity of Sb₃⁻ is estimated to be 1.85(3) eV.

FIG. 7. The 351 nm photoelectron spectrum of Sb₄⁻. Two neutral electronic states are observed (features a and b), and the width of feature a suggests than we can only determine an upper bound on the adiabatic electron affinity, $EA(5b₄⁻) < 1.00(10)$ eV.
TABLE IV. Features in the 351 nm Sb⁻ and Sb⁺ photoelectron spectra. Peak centers and widths are determined by fits to Gaussian line shapes.

<table>
<thead>
<tr>
<th>Label</th>
<th>Assignment</th>
<th>eKE (eV)</th>
<th>Peak width (FWHM, eV)</th>
<th>β</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb⁻</td>
<td>1A₂(C₂v) → 3A₂(D₃h)</td>
<td>1.628</td>
<td>0.131</td>
<td>-0.53</td>
<td>peak</td>
</tr>
<tr>
<td>a</td>
<td>2B₁(C₃v) → 3A₂(D₃h)</td>
<td>1.471</td>
<td>0.127</td>
<td>-0.67</td>
<td>peak</td>
</tr>
<tr>
<td>b</td>
<td>0.25-1.35</td>
<td></td>
<td></td>
<td>0.0</td>
<td>continuous, structureless feature</td>
</tr>
<tr>
<td>c</td>
<td>2A₂m, h → 34m(h)</td>
<td>0.22</td>
<td></td>
<td></td>
<td>peak</td>
</tr>
<tr>
<td>Sb⁺</td>
<td>1A₃-2T₂</td>
<td>1.962</td>
<td>0.480</td>
<td>0.29</td>
<td>peak</td>
</tr>
<tr>
<td>a</td>
<td>1T₁-2T₂</td>
<td>1.058</td>
<td>0.288</td>
<td>-0.15</td>
<td>peak</td>
</tr>
<tr>
<td>b</td>
<td>0.2-0.8</td>
<td></td>
<td></td>
<td>0.0</td>
<td>continuous, structureless feature</td>
</tr>
</tbody>
</table>

The negative-ion ground state is assigned in Table IV as ³A₂, based both on double occupation of the e⁺ highest occupied molecular orbital (HOMO) predicted by theory for Sb⁺ and on Hund's rules.

From the binding energy of the center of peak a, we determine a vertical detachment energy of 1.90(2) eV. The adiabatic electron affinity of Sb⁺ is estimated by assuming that the origin will be shifted from the center of peak a by the same fraction of the linewidth as the similarly shaped and comparably wide band a in the Sb⁻ spectrum, where vibrational resolution permitted rigorous assignment of an origin. The result is an adiabatic electron affinity of 1.85(3) eV.

The photoelectron spectrum of Sb⁻ contains two broad peaks, separated by 0.90 eV. Calculations by Zhang and Balasubramanian at the CASSCF-MRSDCI level predict a T₄g geometry for Sb₄⁺ with a 1A₁ ground state. The HOMO is of e symmetry and the lowest unoccupied molecular orbital (LUMO) is of t₁ symmetry, suggesting a 2T₁ negative-ion ground state. This state will undergo Jahn–Teller distortion, and the absence of electronic hot bands in the photoelectron spectrum indicates that only one component is significantly populated. This seems reasonable, since the photoelectron spectrum of Sb₄ taken by Wang et al. probes the 2T₂ excited state of Sb₄⁺ and indicates that splittings between components can be on the order of 0.4 eV.

Band a is assigned as a transition from the lowest-energy component of the 2T₁ anion ground state to the 1A₁ ground state of Sb₄⁺. The broad contour of band a is indicative of the large geometry change associated with the Jahn–Teller distortion. In the case of a, we might expect roughly equal but opposite geometry changes away from a negative-ion equilateral triangular geometry. Peak d is assigned as a transition from the negative-ion ground state to the first excited state (4A₂⁺) of the neutral. This state is predicted to lie 1.31 eV above the ground state; we measure an excitation energy of 1.4 eV. The negative-ion ground state is assigned in Table IV as ³A₂, based both on double occupation of the e⁺ highest occupied molecular orbital (HOMO) predicted by theory for Sb⁺ and on Hund's rules.
From the peak center of band a, we determine a vertical detachment energy of 1.57(5) eV. The broadness of band a causes difficulties in the determination of an adiabatic electron affinity. The geometry changes involved are likely to be so large that the vibrationless origin is not visible. Wang et al.\textsuperscript{17} observed bands of similar width (also vibrationally unresolved) in transitions from the \(^1A_1\) ground state of Sb\(_4^-\) to the \(^2E\) ground state of Sb\(_2^+\). Their models of these bands led to an estimate of the adiabatic ionization potential (IP) at approximately 1.2 eV below the vertical IP. The Sb\(_4^-\) spectrum does not contain sufficient information for analogous modeling, since the Jahn–Teller splittings of the anion \(^2T_1\) state are not determined and lack of vibrational resolution precludes determination of the relative roles of the two symmetry-allowed normal coordinates in the distortion. We report the lowest photoelectron energies detectable above the inherent noise level as an upper bound for the electron affinity, \(\text{EA(Sb}_4^-) < 1.00(10)\) eV.

In light of these findings for the EA of Sb\(_4^-\), we suggest a new interpretation of our previously reported\textsuperscript{2} photoelectron spectrum of Bi\(_4^-\). The photoelectron onset for Bi\(_4^-\), which was previously assumed\textsuperscript{2} to correspond to the electron affinity, should rather be regarded as an upper bound, resulting in \(\text{EA(Bi}_4^-) < 1.05(10)\) eV.

Band b can be assigned as a transition to the lowest-energy component of the \(^3T_2\) excited state of the neutral. Zhang and Balasubramanian\textsuperscript{15} calculate the state (with undistorted \(T_d\) geometry) to be the lowest excited electronic state of Sb\(_4^-\) at 2.57 eV above the ground state. We observe a vertical detachment energy to this state that is 0.9 eV above that to the ground state. Because band b is narrower than band a, the band center of band b lies closer to its vibrationless origin than the band center of band a, and the difference in vertical energies of 0.9 eV will be lower than the term energy of the excited state. If we estimate the origin of band b to lie at an eKE of 1.2 eV, and assume that the origin of band a is shifted by a maximum of 1.2 eV from the intensity maximum, we obtain an excitation energy in the range 1.3–2.0 eV, significantly lower than the calculated value of 2.57 eV. As is suggested by Zhang and Balasubramanian, the low excitation energy of this state compared to the calculation is probably due to Jahn–Teller stabilization. The narrowness of band b compared to a is indicative of the similarity of the geometries of the lowest components of the \(^2T_1\) anion and \(^3T_2\) neutral states. Since the transition of band b results from the removal of an electron from a bonding \(e\) orbital we expect and observe substantial geometry change; however, it appears that both states are distorted away from the \(T_d\) geometry in a similar fashion.

In both the Sb\(_3^-\) and Sb\(_4^-\) spectra we observe a broad continuous feature, labeled c, which we cannot adequately explain. A similar feature was observed\textsuperscript{2} in the photoelectron spectrum of Bi\(_3^-\). Laser fluence tests showed that the Sb\(_3^-\) and Sb\(_4^-\) features were due to a one-photon process. One possibility is that we are accessing highly vibrationally excited states of geometries that differ from the equilibrium \(D_{2h}\) and \(T_d\) structures of the trimer and tetramer. Calculations have not been performed on the stabilities of electronic states that differ from these symmetric structures.

### D. Photoelectron angular distributions

The anisotropy parameters for photoelectron angular distributions in the 351 nm spectra of Sb\(_-\), Sb\(_3^-\), and Sb\(_4^-\) are listed in Tables I and IV. They are measured with an accuracy of approximately \(\pm 0.1\). For each of these spectra, the anisotropy parameters of the peaks increase with increasing electron kinetic energy. In the eKE region of these spectra this is typical behavior for atomic \(p\) electron detachment,\textsuperscript{33} and is similar to the behavior seen\textsuperscript{2} for Bi\(_-\) and Bi\(_3^-\).

On the other hand, the Sb\(_3^-\) angular distributions are very unusual. In the case of direct, nonresonant electron detachment, the anisotropy parameter does not vary significantly over a single electronic transition. For the 351 and 364 nm Sb\(_3^-\) photoelectron spectra, the presence of a resonace causes large changes in angular distributions through the progressions. Table V shows the range of anisotropy parameters observed for different vibrational peaks in bands a, c, and d in both the 351 and 364 nm spectra. For feature b, the signal was too weak for accurate determination of the anisotropy parameter. For the 351 nm

<table>
<thead>
<tr>
<th>Band</th>
<th>eKE in the 351 nm spectrum (eV)</th>
<th>Range of (\beta) in the 351 nm spectrum*</th>
<th>Range of (\beta) in the 364 nm spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>0.3–0.6</td>
<td>(-0.3 \rightarrow -0.7)</td>
<td>(+0.1 \rightarrow -0.1)</td>
</tr>
<tr>
<td>c</td>
<td>0.9–1.15</td>
<td>(0.0 \rightarrow -0.55)</td>
<td>(+0.1 \rightarrow -0.1)</td>
</tr>
<tr>
<td>a</td>
<td>2.0–2.3</td>
<td>(+0.3 \rightarrow -0.2)</td>
<td>(+0.7 \rightarrow -0.2)</td>
</tr>
</tbody>
</table>

* Higher \(\beta\) values tend to be toward the lower eKE side of each band (see Fig. 8).

FIG. 8. Bands a, c, and d of the 351 nm photoelectron spectrum of Sb\(_3^-\) taken at laser polarizations parallel and perpendicular to the electron ejection direction. The intensities of the parallel and perpendicular spectra are plotted on the same intensity scale; however, the intensities of band a are not to scale with respect to those of bands c and d. The change in band profiles between the two laser polarizations illustrates the variation in anisotropy parameter across a single band (see Table V), and is a signature of resonant photodetachment.

TABLE VI. Electron affinities (eV) of group V atoms, dimers, trimers, and tetramers.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom</th>
<th>Dimer</th>
<th>Trimer</th>
<th>Tetramer</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>(-0.5)</td>
<td>(-0.0)</td>
<td>2.68(1)</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.7465(3)</td>
<td>0.589(25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.81(3)</td>
<td>0.70(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>1.046(3)</td>
<td>1.282(8)</td>
<td>1.85(3)</td>
<td>&lt;1.00(10)</td>
</tr>
<tr>
<td>Bi</td>
<td>0.946(10)</td>
<td>1.271(8)</td>
<td>1.60(3)</td>
<td>&lt;1.05(10)</td>
</tr>
</tbody>
</table>

*Reference 35.
1Reference 36.
2Reference 39.
3Reference 37.
4Our interpretation of data in Feldmann et al. (Ref. 38).
5This work.
6Reference 2.
7Reinterpretation of the value in Ref. 2 as an upper bound.

The electron affinities in Table VI show that for As$_2$ and P$_2$ the dissociation energy decreases upon addition of an electron, the anticipated result for addition into an antibonding orbital. On the other hand, the dissociation energies of Bi$_2$ and Sb$_2$ increase upon electron addition, although the changes in equilibrium properties (bond length and vibrational frequency) behave in accord with addition into an antibonding orbital. From Eq. (2) and the Sb$_2$ dissociation energy $E(D_0(Sb_2)) = 71.2 \pm 1.0$ kcal/mol (3.09 \pm 0.04 eV) determined from mass-spectrometric measurements of high-temperature equilibria, we determine an Sb$_2^-$ dissociation energy, $D_0(Sb_2^-) = 76.8 \pm 1.0$ kcal/mol (3.33 \pm 0.04 eV).

IV. CONCLUSIONS

We have reported the 351 nm laser photoelectron spectra of small antimony cluster anions, obtaining the electron affinities (Table VI) of antimony atom, dimer, and trimer, and an upper bound for the electron affinity of antimony tetramer. The electron affinities of the antimony clusters are very similar to those recently reported for the small clusters of bismuth, another group V metal. All of the spectra display electronic structure, which is vibrationally resolved only for the dimer. The observed electronic structure can be explained in terms of high-level ab initio calculations by Balasubramanian and co-workers.

The Sb$_2^-$ spectrum displays unusual intensities and photoelectron angular distributions which indicate that photodetachment is mediated by an autodetaching resonance that is accessed at the photodetachment wavelength (351 nm). These unusual effects are enhanced when the wavelength is changed to 364 nm. This study and other recent negative-ion photoelectron spectra show that the possibility of an accidental resonance must always be a consideration in the interpretation of a photoelectron spectrum.

Note added in proof: In Ref. 2, the ground electronic state of $D_{3a}$ bismuth trimer mentioned throughout Secs. III C and III E should be $^2E''$, not $^2E'$. The resulting spin-orbit components in the $D_{3a}$ double group are then $E_{1/2}$ and $E_{3/2}$, not $E_{2/2}$ and $E_{5/2}$. The authors thank Dr. J. Berkowitz and Professor K. Balasubramanian for calling attention to this error.
ACKNOWLEDGMENTS

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1 For example, Metal Clusters, edited by M. Moskovits (Wiley Interscience, New York, 1986), and references therein.
7 The most precise constants for the X and B states of Sb2 are in G. Gerber and G. Kuscher, Chem. Phys. 60, 119 (1981).
24 Electronic state assignments are given in Hund’s case a (case c) notation, i.e., \( \Sigma^\pm \Omega^\pm \), where \( \Omega \) designates parity (gerade or ungerade).
32 K. Balasubramanian (private communication).
38 D. Feldmann, R. Rackwitz, H. J. Kaiser, and E. Heinicke, Z. Naturforsch. A 32, 600 (1977). The value we quote for the electron affinity of As2 is based on our own interpretation of the photodetachment threshold data in this publication, where we assume that the thresholds are at the electron affinities. Similar interpretation of the thresholds for P2 and S2 data in the same publication leads to electron affinities that are within ±0.05 eV of the more accurate values later measured by laser photoelectron spectroscopy.