

Anion photoelectron spectroscopy of small indium phosphide clusters (In_xP_y^- ; $x, y=1-4$)

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Small indium phosphide clusters having 2–8 atoms are studied using anion photoelectron spectroscopy of In_xP_y^- ($x, y=1-4$). From these spectra, the electron affinities are determined. Both ground and low-lying excited electronic states of the neutral clusters are observed. An electronic gap is shown in the even cluster anion spectra.

The electronic and vibrational spectroscopy of semiconductor clusters has been an extremely active area in physical chemistry, as it offers an opportunity to learn how the properties of matter evolve from the molecular limit to the larger size regimes which are of interest in technological applications. A vital component in experimental studies of these species is the ability to combine size selectivity with spectral resolution, so that one can follow the dependence of the electronic and vibrational structure of clusters as a function of size. Three techniques which have proved particularly valuable in probing the spectroscopy of semiconductor clusters are (i) photodissociation spectroscopy,^{1,2} in which one records the depletion of a cluster of a given mass as a function of dissociation wavelength, (ii) negative ion photodetachment spectroscopy, in which the photoelectron spectrum³⁻⁵ or (at higher resolution) the zero electron kinetic energy (ZEKE) spectrum^{5,6} of a size-selected anion cluster probes the electronic and vibrational structure of the resulting neutral species, and (iii) Raman spectroscopy of size-selected clusters deposited onto a matrix.⁷ In this Communication, we report the photoelectron spectra of a series of size-selected indium phosphide cluster anions.

While much of the experimental and theoretical work thus far on semiconductor clusters has focused on pure elemental clusters of silicon and germanium, mixed semiconductor clusters are also intriguing targets for study due to their greater complexity. Smalley and co-workers^{4,8} have performed photoionization and photodetachment experiments on gallium arsenide clusters, finding that clusters with an odd number of atoms consistently have lower ionization potentials and higher electron affinities than even clusters. Several theoretical groups have carried out *ab initio* studies of gallium arsenide and other mixed clusters.⁹⁻¹³ Mandich and co-workers¹ have performed a photodissociation spectroscopy study of indium phosphide clusters ranging in size from 5–14 atoms. The spectra showed the rising edge of an electronic absorption band which was typically quite close to the band gap of bulk crystalline indium phosphide, 1.34 eV at 300 K.¹⁴ These striking results, which suggest that very small indium phosphide clusters exhibit properties reminiscent of the bulk material, motivate the work described in this Communication. We report the photoelectron spectra of indium phosphide cluster anions having 2–8 atoms (In_xP_y^- , $x, y=1-4$). We determine the electron affinities from

the photoelectron spectra, and observe both ground and low-lying excited electronic states of the neutral clusters.

The apparatus used in the present work is a fixed-frequency negative ion photoelectron spectrometer that has been described in detail elsewhere.¹⁵ Indium phosphide cluster anions are generated in a laser vaporization source by focusing the second harmonic (532 nm) of a YAG laser onto a rotating and translating indium phosphide rod. The resulting plasma is entrained in a pulse of helium carrier gas from a piezoelectric valve, and expanded through a clustering channel into the source vacuum chamber of the spectrometer. The anions generated in the plasma are extracted into a time-of-flight mass spectrometer and accelerated to an energy of about 1 keV. The ions separate according to mass and are detected by a microchannel plate detector. The resulting ion beam is crossed by a second pulsed YAG laser beam. By controlling the laser firing time, the cluster ion of interest is selectively detached. The kinetic energy of the photoelectrons is determined via their time-of-flight. The instrumental resolution is 8–10 meV for an electron kinetic energy (eKE) of 0.65 eV and degrades as $(\text{eKE})^{3/2}$.

Figure 1 shows the mass spectrum of the indium phosphide cluster anions. An interesting feature in Fig. 1 is that four of the five most intense peaks correspond to anions with five atoms, namely, P_5^- , InP_4^- , In_2P_3^- , and In_3P_2^- . This suggests that these anions are particularly stable.

Figure 2 shows the 16 photoelectron spectra of indium phosphide clusters ranging from InP^- to In_4P_4^- . The electron kinetic energy (eKE) is given by

$$\text{eKE} = h\nu - \text{EA} - E^{(0)} + E^{(-)},$$

where $h\nu$ is the photon energy (4.657 eV), EA is the electron affinity of the neutral cluster, and $E^{(0)}$ and $E^{(-)}$ are the internal (electronic+vibrational) energies of the neutral and anion, respectively. The spectra show resolved peaks, most of which represent transitions from the anion ground electronic state to various electronic states of the neutral. In the In_2P_2^- spectrum, for example, the peaks labeled as X, A, and B correspond to transitions to the In_2P_2 ground state and first two excited electronic states, respectively. The onset of band X yields the adiabatic electron affinity.

Some of the smaller features in Fig. 2 require additional explanation. There is a pair of small peaks (labeled with *) at the same electron kinetic energy of 2.865 and 2.985 eV in the

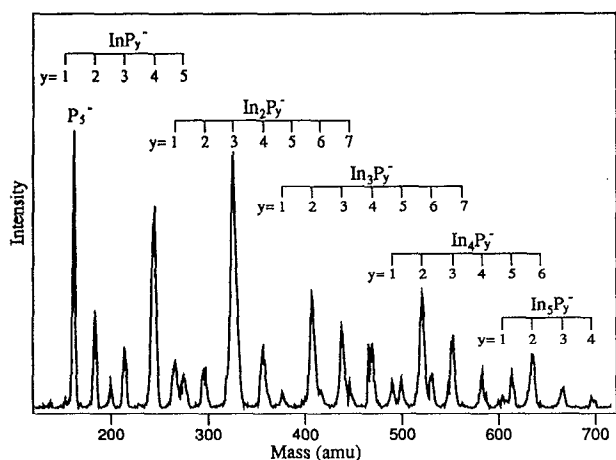


FIG. 1. Mass spectrum of indium phosphide anion clusters ranging in mass from 130–700 amu.

photoelectron spectra of the larger In_xP_y^- anions. These are most likely due to a two-photon absorption process, in which the first photon dissociates these clusters into the same daughter anion which is subsequently photodetached by the second photon. The electron binding energy of this daughter anion is 1.69 eV. It therefore cannot be In^- or P^- [$\text{EA}(\text{In})=0.30$ eV, $\text{EA}(\text{P})=0.7465$ eV¹⁶], and a comparison with the other spectra in Fig. 2 shows that it is not InP^- or In_2P^- . Based on the smallest clusters which show this feature, the remaining possibility is In_2^- , for which no photoelectron spectrum exists. However, the splitting of 120 meV between the two peaks is in good agreement with the calculated energy separation of 129 meV between the $^3\Pi_u$ ground electronic state and the $^3\Sigma_g^-$ first excited state of In_2 .¹⁷

The other anomalous feature is the broad peak around $\text{eKE}=3.8$ eV in the InP_2^- spectrum. The intensity of this peak depended upon the source conditions and it was not observed when the expansion carrier gas was changed from helium to argon; we therefore assign this band to the transition from a low-lying electronic state of the InP_2^- anion. Peaks similar in appearance to this in other spectra (such as the highest electron kinetic energy peak in the In_2P_4^- spectrum) were insensitive to source conditions and are therefore assigned to transitions between the anion and neutral ground states.

The adiabatic electron affinities of the neutral clusters were determined as the energy difference between the photon energy and onset of the leading edge of the highest kinetic energy band in the photoelectron spectrum (with the excep-

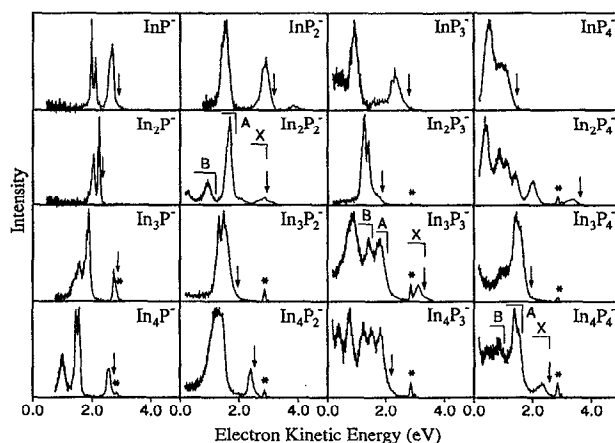


FIG. 2. Photoelectron spectra of 16 In_xP_y^- ($x,y=1-4$) clusters at 4.657 eV photodetachment energy. Arrows indicate electron kinetic energies corresponding to adiabatic electron affinities, and the asterisks indicate the two-photon peaks generated by In_2^- .

tion of the cases just discussed). In some cases, notably In_3P_3^- , the exact onset is unclear because the band tails off slowly towards high electron kinetic energy; these tails are attributed to vibrationally hot anions. The best estimates for the true onsets are indicated by arrows in Fig. 2, and the corresponding electron affinities are listed in Table I. Table I shows that clusters having an even total number of atoms have smaller electron affinities than the adjacent odd clusters; the only exceptions are InP_2 and In_4P (see below). Table I also shows that, for the five atom clusters, the electron affinity increases with phosphorus content, reaching a maximum value of 3.8 eV for P_5 (not listed in Table I). The high electron affinities for In_2P_3 , InP_4 , and P_5 are consistent with the intense anion peaks in the mass spectrum.

The second general trend is that, for all the even clusters, there is a noticeable gap between the bands corresponding to transitions to the ground and first excited states of the neutral. This gap is absent in all of the odd cluster spectra except for InP_2 and In_4P . Figure 3 shows these gaps for clusters with four, six, and eight atoms. The gaps range from 0.75–1.6 eV, and for clusters with the same number of atoms, the gap decreases as the number of indium atoms increases.

Both general trends can be explained if the neutral, even clusters are closed-shell species with a substantial highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap while odd clusters are open-shell radicals. This is precisely what has been predicted in the

TABLE I. Adiabatic electron affinities of indium phosphide clusters In_xP_y ($x,y=1-4$) determined in the present work. The values are estimated to be accurate to ± 0.05 eV.

Cluster	Electron affinity (eV)	Cluster	Electron affinity (eV)	Cluster	Electron affinity (eV)	Cluster	Electron affinity (eV)
InP	1.95	InP_2	1.61	InP_3	1.86	InP_4	3.22
In_2P	2.36	In_2P_2	1.68	In_2P_3	2.72	In_2P_4	1.08
In_3P	1.77	In_3P_2	2.07	In_3P_3	1.30	In_3P_4	2.72
In_4P	1.88	In_4P_2	2.00	In_4P_3	2.43	In_4P_4	2.07

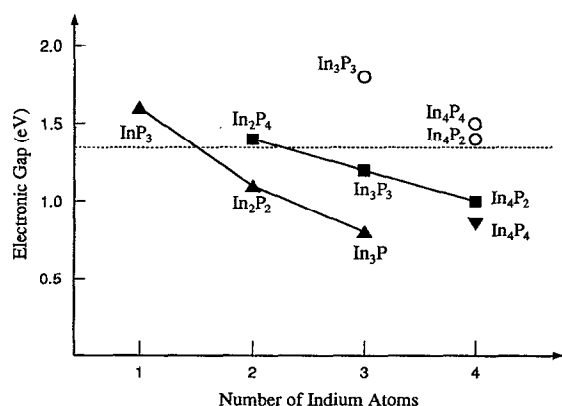


FIG. 3. Electronic gaps in the even-numbered indium phosphide clusters. \blacktriangle : four-atom clusters, \blacksquare : six-atom clusters, \blacktriangledown : eight-atom clusters. Dotted line indicates the bulk band gap of indium phosphide (1.34 eV) (Ref. 14). Absorption onsets reported by Mandich (Ref. 1) are indicated by \circ .

ab initio calculations by Lou *et al.*¹² on gallium arsenide clusters. Thus, an even cluster anion is formed by adding an electron to the LUMO of the neutral cluster, whereas in an odd cluster anion, the added electron goes into a half-filled valence orbital. Hence, the even clusters have a smaller electron affinity than the odd clusters. This simple picture also explains the electronic gap in the even cluster anion spectra. The ground state of the neutral is formed by removal of the LUMO electron, while the first excited state is formed by removal of an electron from the HOMO. Hence the gap in the photoelectron spectrum should, to first order, correspond to the HOMO–LUMO gap in the neutral cluster. In contrast, photodetachment of an odd cluster anion cannot access the LUMO of the neutral cluster by a one-electron transition, so the photoelectron spectrum should look quite different.

It is instructive to compare our results to the photodissociation experiments of Mandich¹ in more detail. The latter experiments probed the energy range from 1.0–1.8 eV for clusters ranging in size from 5–14 atoms; all the clusters studied showed the onset of an electronic absorption band in this energy range. In contrast, the anion photoelectron spectrum maps out the ground and excited states of the neutral cluster over a wider energy range, typically 2–3 eV depending on the electron affinity of the cluster. For the even clusters studied by both methods (In_4P_2^- , In_3P_3^- , and In_4P_4^-), Figure 3 shows that the gap in the photoelectron spectrum between the ground and first excited states is noticeably less than the onset observed in the photodissociation experiments. However, the gap between peaks X and B in the In_3P_3^- and In_4P_4^- spectra is 1.9 and 1.5 eV, respectively, which is much closer to the onsets in Mandich's experiments. A possible explanation for this is that peaks A and B in our spectra correspond to transitions to triplet and singlet excited states, respectively. The triplet states would not be seen in the photodissociation experiments if the $\Delta S=0$ selection rule applies. In the In_4P_2^- spectrum, the large peak below 2.0 eV appears anomalously broad, suggesting that it is composed of two or more overlapping transitions terminating in the analogous triplet and singlet excited states.

A comparison of the odd cluster spectra obtained by the

two methods is more problematic. The onsets in the photodissociation spectra presumably correspond to a transition between one of the valence orbitals to the LUMO, but the resulting upper state is not accessible from the anion by a one-electron transition. The peaks in the photoelectron spectrum correspond instead to removal of electrons from the various valence orbitals of the anion. Some of the excited neutral states generated by such a transition should be optically accessible from the neutral ground state but at a lower frequency than could be reached with the lasers used in the photodissociation work. It would be interesting to perform the two-color photodissociation experiments using a lower frequency infrared laser as the first excitation pulse to see which, if any, of the low-lying states in the photoelectron spectra appear.

The results of the photodissociation experiments indicate that the HOMO–LUMO gap in these very small clusters is similar to the bulk band gap in indium phosphide. In bulk indium phosphide, the band gap transition corresponds to a transition between a $p\sigma$ bonding orbital with dominant P character and a nonbonding $s\sigma$ orbital largely localized on the In atoms.¹⁸ The photodissociation experiments imply that similar transitions occur in very small indium phosphide clusters, even though a high percentage of the atoms are “surface” atoms, suggesting that In–P bonding is the dominant chemical interaction in these clusters. Our results are in qualitative agreement in that the even cluster anion photoelectron spectra reveal the existence of electronic states at energies close to those seen in the photodissociation spectra. However, the photoelectron spectra cover a considerably wider range of energies, and they demonstrate that the electronic structure in these clusters is more complex than implied by the photodissociation experiments.

Finally, we consider the InP_2^- and In_4P^- clusters which, as mentioned above, deviate from the observed even–odd trends; their electron affinities are anomalously low and they exhibit a significant electronic gap. We have recently obtained a vibrationally resolved zero electron kinetic energy spectrum of InP_2^- (Ref. 19) which suggests that the InP_2^- neutral and anion are acute C_{2v} structures with the In atom bound to a P_2 unit, an interpretation consistent with *ab initio* calculations on isovalent GaAs_2^- and GaAs_2^- .¹¹ Given that P–P bonding may be stronger than In–P bonding for these species, one can understand how the photoelectron spectrum might differ significantly from the other clusters. In In_4P^- , one might also expect that In–In interactions outweigh effects due to In–P bonding. Hence, both exceptions can be rationalized in that In–P bonding may not be the dominant chemical interaction in the anion and neutral clusters.

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