

Probing the connection between cluster and bulk electronic structure of InP using vacuum ultraviolet anion photoelectron spectroscopy

Giovanni Meloni, Michael J. Ferguson, Sean M. Sheehan, Harry Gomez¹,
Zhuan Liu², Daniel M. Neumark^{*}

*Department of Chemistry, University of California, Berkeley, CA 94720, USA
Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

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Abstract

Vacuum ultraviolet photoelectron (PE) spectra of In_xP_x^- ($x = 2\text{--}13$) clusters were measured to probe the evolution of their electronic structure with size. The spectra of smaller ($x \leq 6$) clusters show numerous discrete electronic features, with fewer seen for $x = 7$ and 8. For $x \geq 9$, the PE spectra comprise two broad peaks resembling the first two valence bands of the InP bulk photoemission spectrum and calculated density of states. Electronic structure calculations show that the character of the electronic states contributing to the two bands in the cluster PE spectra is similar to that in the bulk photoemission spectrum.
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Atomic and molecular clusters have attracted tremendous attention because of the unique role they play as bridge between isolated atoms and condensed matter [1]. Semiconductor clusters and nanocrystals are of particular interest because of their size-dependent electrical, optical, photocatalytic, and nonlinear optical properties [2–4]. A fundamental understanding of how the electronic states of such clusters vary with size is one of the central goals of cluster science. While the evolution of semiconductor electronic structure from the nanocrystalline to bulk regimes is now reasonably well understood [5], this size-dependence is more complicated in smaller clusters closer to the molecular limit. In this Letter, we present photoelectron spectra of size-selected InP cluster anions at 157 nm in order to map out their electronic structure and to probe the size regime over which molecular features begin to resemble those of the bulk material.

Photoelectron spectroscopy (PES) has a rich history in the field of semiconductor physics. Much of our knowledge of valence and core band structure in semiconductors derives from ultraviolet and X-ray PES [6,7], with angle-resolved measurements in particular playing a key role in elucidating band structure [8]. PES has also been used to examine size-dependent effects in the valence band of nanocrystals [9,10], complementing information obtained from optical and tunneling spectroscopy [11]. In the gas phase, PES of semiconductor anion clusters has been shown to be a powerful means of mapping out the electronic structure of the neutral clusters generated by photodetachment [12].

Anion PE spectra of mixed group 13–15 clusters have been reported previously, including studies by Smalley's group [13] and our group of GaAs clusters [14], and experiments by our group on AlP [15], GaP [14,16], and InP clusters [17,18]. These investigations yielded size-dependent electron affinities, vertical detachment energies to neutral excited states, and, for the smaller clusters, vibrationally resolved features [14,15] which could be compared directly with electronic structure calculations. However, the connection between experimental results

^{*} Corresponding author. Fax: +15106423635.

E-mail address: dan@radon.cchem.berkeley.edu (D.M. Neumark).

¹ Present address: Intel Corporation, Hillsboro, OR 97124, USA.

² Present address: Nanometrics, INC, Milpitas, CA 95035, USA.

on small semiconductor clusters and phenomena associated with bulk band structure has proved elusive. Early anion PES [17] and photodissociation experiments [19] on stoichiometric In_xP_x clusters yielded HOMO–LUMO gaps that were close to the bulk band gap, suggesting, for example, that the excess electron in the cluster anions resided in the cluster analog of the conduction band, but this result appears to have been fortuitous. It is more likely that the extra electron in the anion does not reside in a delocalized conduction band analog, but rather in a localized surface state. As a result, one cannot readily extract the analog of a bulk band gap from the PE spectra of InP cluster anions. A similar holds for silicon clusters [20], although negative ion PES does yield the cluster analog of the band gap in Hg_n and Mg_n clusters [21,22].

In this Letter, we undertake a different approach to connecting cluster PE spectra to bulk properties. By photodetaching InP cluster anions with as many as 26 atoms further into the vacuum ultraviolet (157 nm, or 7.9 eV, compared to our previous work at 266 nm), we can probe more tightly bound cluster orbitals and make a more detailed comparison with the valence band structure gleaned from bulk photoemission spectra. Wang and co-workers [23,24] have demonstrated this approach to be quite productive in PES studies (at lower photon energies) of transition metal clusters.

Details of our PES apparatus have been discussed elsewhere [25]. We have, however, added a magnetic bottle electron energy analyzer [26] to expand the capabilities of the instrument. In_xP_y^- ($x = y$ for stoichiometric clusters) clusters were produced by means of a pulsed laser ablation (at 532 nm) of an InP disk coupled to a pulsed supersonic beam of Ar carrier gas. The cluster anions were mass-analyzed with a linear reflectron time-of-flight mass spectrometer for which $m/\Delta m \approx 2000$ at an average beam energy of 3.75 keV, and photodetached with a pulsed, fixed frequency, F_2 excimer laser (GAM EX50F), 157 nm and 2 mJ/pulse, with unstable resonator optics.

Photoelectron kinetic energies (eKE's) were determined by time-of-flight measurements using a magnetic bottle analyzer based on the designs by Cheshnovsky et al. [26] and Wang et al. [27]. The mass-selected clusters are not decelerated before interaction with the laser. The instrumental resolution is estimated at 0.15 eV for In_6P_6^- at an electron kinetic energy (eKE) of 1 eV. The magnetic bottle region consists of two parts: a strong permanent magnet adjustable in height below the photodetachment zone and a 1.2 m long solenoid. The distance of the permanent magnet from the ion beam and the strength of the magnetic field at the center of the solenoid were chosen to optimize the signal-to-noise ratio. All spectra shown here were background-subtracted to eliminate the contribution from electrons

produced by stray 157 nm photons interacting with surfaces near the interaction region.

Fig. 1 shows the 157 nm PES spectra of stoichiometric In_xP_x clusters with $x = 2–13$. All PE spectra are plotted as a function of electron binding energy (eBE), defined as $\text{eBE} = h\nu - \text{eKE}$, where $h\nu$ is the photon energy (7.9 eV at 157 nm). The spectra show several distinct bands corresponding to different electronic states of the neutral cluster. They were calibrated by comparing the features at low eBE with those obtained in our previous study of InP clusters at 266 nm using a field free time-of-flight analyzer [18]. All features in Fig. 1 at $\text{eBE} > 4.7$ eV (vertical line) are new features that could not be observed at 266 nm.

The In_xP_x^- spectra in Fig. 1 exhibit several size-dependent trends. The spectra for $x \leq 6$ show numerous discrete electronic features corresponding to various electronic states of the neutral cluster, and exhibit significant differences as the size of the cluster is varied. The number of resolved features drops for $x = 7$ and 8, and for $x \geq 9$, there is a coalescence of features, so that the PE spectra comprise two broad peaks whose shapes change only slightly with increasing cluster size. The main size effect from $x = 9$ to 13 is a small increase in vertical detachment energy (VDE), corresponding to the maximum of the peak at lower eBE; the VDE increases from 4.2 eV for $x = 9$ to 4.4 eV for $x = 13$. In this size regime, the PE spectra are also largely independent of

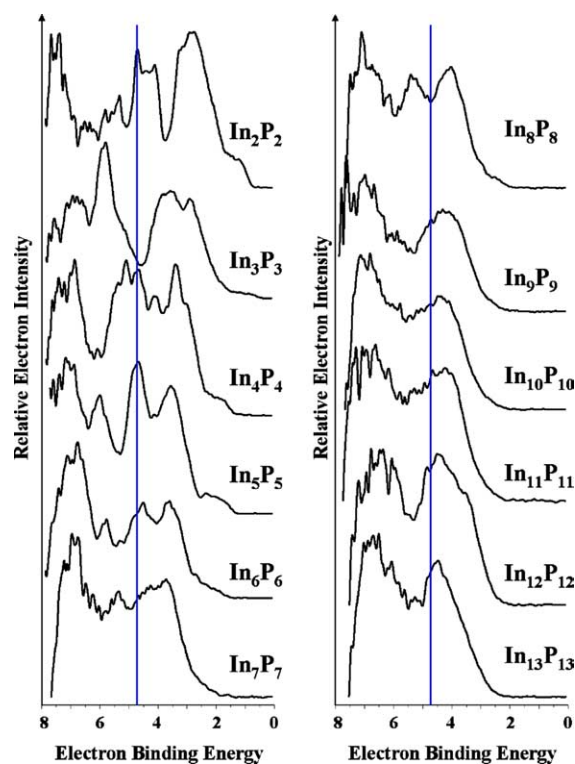


Fig. 1. Anion photoelectron spectra of size-selected stoichiometric In_xP_y^- ($x = 2–13$) clusters at 7.9 eV detachment energy.

stoichiometry; PE spectra taken for In_9P_x^- ($x = 7, 8$) and $\text{In}_{10}\text{P}_x^-$ ($x = 8, 9$) are essentially the same as those for the stoichiometric clusters.

In photoemission experiments on semiconductor surfaces [7], the photoelectron kinetic energy distribution reflects the density of states (DOS) in the valence and core bands of the bulk material. In the InP photoemission spectrum [6], the highest energy band, whose maximum lies about 2 eV below the valence band (VB) edge, is composed primarily of linear combinations of phosphorus 3p-orbitals, while the next band with maximum at -6 eV is a mix of indium 5s-like states and phosphorus 3p-like states [28]. Our PE spectra for In_xP_x^- , $x \geq 9$, are quite similar to the photoemission spectrum. The two peaks in the anion PE spectra are closer together, i.e. their maxima are separated by 2.5–3 eV compared to 4 eV in the photoemission spectrum. Nonetheless, there appears to be a correspondence between features in the anion cluster PE spectra and the bulk photoemission spectra.

In order to address this issue in more detail, electronic structure calculations were carried out to learn more about the geometries and the nature of the molecular orbitals of InP clusters in the size range studied here. We performed density functional calculations on In_3P_3 , In_4P_4 , In_6P_6 , and In_9P_9 at the B3LYP (Becke three-parameter exchange functional with the Lee, Yang, and Parr correlation functional) level of theory. We used the GAUSSIAN 98 program suite [29] with a correlated consistent polarized valence double-zeta (cc-pVDZ) basis set for P atoms and a Los Alamos National Laboratory double-zeta (LANL2DZ) with effective core potential (ECP) basis set for In atoms. Many starting geometries were used and only the lowest energy structures are shown in Fig. 2. All vibrational frequencies for these structures were found to be real, indicating they are at least local minima, but we cannot rule out the possibility of lower-lying isomers that were missed by the optimization procedure. There are not significant changes between anion and neutral geometries. The structures in Fig. 2 clearly do not resemble the zinc-blende structure of bulk InP. Indeed, if a zinc-blende initial geometry is used for In_9P_9 , the dangling bonds disappear and the structure is optimized to maximize the coordination number of each atom.

Our calculated lowest energy geometry for In_3P_3 is almost identical to the work by Costales et al. [30]. The structures for In_4P_4 , In_6P_6 , and In_9P_9 are here described for the first time. In_4P_4 and In_6P_6 can be compared to calculations on other group 13–15 semiconductor clusters, such as Ga_4As_4 [31–33] and Ga_6As_6 [32,34]. Our In_4P_4 structure has a bicapped octahedral structure with the apex P atoms separated by 2.3 Å, and the four In atoms separated by 3.7 and 4.0 Å. It differs from the lowest energy structures for Ga_4As_4 found by Song et al. [31] and BelBruno [33]; In_4P_4 local minima were located

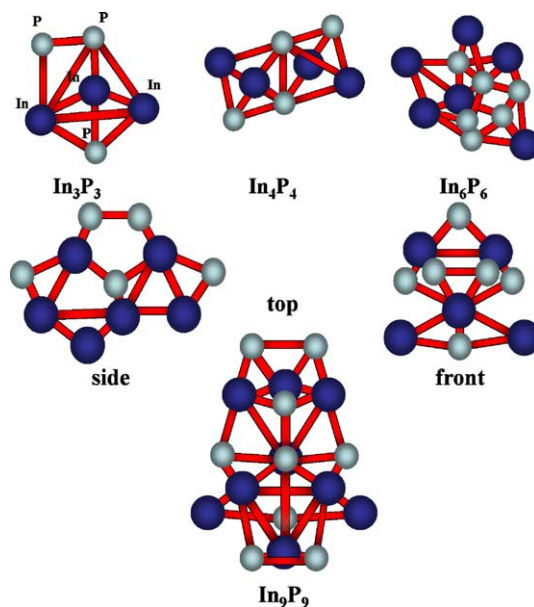


Fig. 2. Structures of the In_3P_3 , In_4P_4 , In_6P_6 , and In_9P_9 clusters optimized at the B3LYP level of theory.

corresponding to those structures and were found to lie 2.1 and 0.6 eV, respectively, higher in energy than our lowest-energy neutral configuration, whereas for the anion these structures lie 0.4 and 0.2 eV above the ground state. In_6P_6 has a distorted C_1 structure, quite different from the Ga_6As_6 molecular arrangements [32,34]. In_9P_9 has a C_s structure with an average In-P bond distance of 2.6 Å. This structure is a nearly prolate symmetric top, with an asymmetry parameter $\kappa = (2B - A - C)/(A - C) = -0.88$, where A , B , and C are the three rotational constants (in decreasing order) for the equilibrium geometry and $\kappa = -1$ is the limit for a prolate top. In contrast, the smaller clusters are nearly oblate, with $\kappa = 0.98$ for In_4P_4 .

The DFT calculations can be used to interpret the trends in electronic structure revealed by the PE spectra, in particular the coalescence of many bands for the smaller clusters into two bands for the larger ones. We analyzed the character of the molecular orbitals (MO) for two cases: In_4P_4 and In_9P_9 . Koopman's Theorem was used to obtain binding energies for electrons in each MO of the anion as an approximate means of determining the vertical detachment energy to the ground and multiple excited states of the neutral cluster, using the lowest energy geometries shown in Fig. 2.

In Fig. 3, stick spectra indicating MO binding energies in the 0–7.9 eV range are superimposed on the PE spectra. In the case of In_4P_4^- , the binding energy of the electron that resides in the singly occupied molecular orbital (SOMO) is considerably less than the next most weakly bound electron. We can identify detachment from the SOMO with the weak shoulder at low binding energy in the experimental PE spectrum (resolved as a

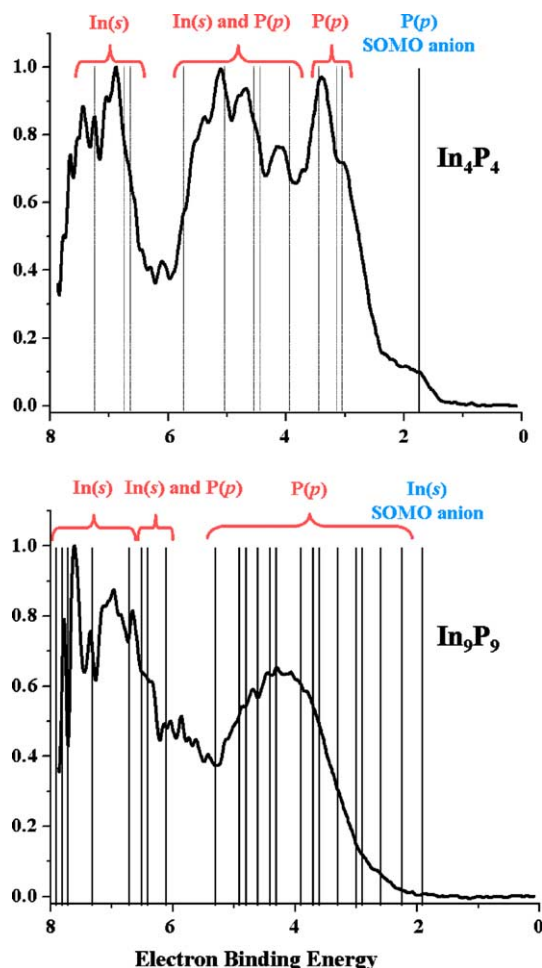


Fig. 3. Superimposition of calculated stick spectra for the electronic transitions of In_4P_4 and In_9P_9 on the anion PE spectra taken using 157 nm photon energy.

distinct peak in our earlier work [17]), and have therefore shifted the calculated stick spectrum by 1.2 eV towards lower eBE to line up the SOMO binding energy with this shoulder. We then observe a reasonable correlation between the remaining calculated binding energies and features in the PE spectrum. The features around 3.1 eV are from detachment from MOs with predominant phosphorous 3p, character, those from 4 to 6 eV correspond to MOs with mixed In 5s and P 3p character, and the feature around 7 eV from MOs with predominant In 5s character.

For In_9P_9 , no shift was applied to the calculated stick spectrum. The MO binding energies segregate into two groups that match reasonably well with the experimental spectrum. Comparison of the stick and PE spectra suggests that the lower energy peak comprises MOs of P (3p) character, while the MOs corresponding to the higher energy peak are a combination of mixed In(5s)/P(3p) and largely pure In(5s) orbitals. This is the same orbital parentage responsible for the first two bands in the bulk photoemission spectrum of InP [28]. It

therefore appears that two features in the In_xP_x^- ($x \geq 9$) PE spectra and the first two bands in the bulk photoemission spectra are of similar origin.

As mentioned above, the splitting between the two bands in the cluster PE spectra is somewhat smaller than in the bulk photoemission spectra. One possible explanation is that only the upper part of the more strongly bound band can be detached at 7.9 eV. However, our electronic structure calculations show no additional states lying at slightly higher binding energies. In fact, the calculations for In_9P_9 show a significant gap until around 10.6 eV, where a new band with predominant P(3s) character is seen, analogous to the third band of the bulk photoemission spectrum [6].

Another possible explanation for the different band spacings could be that the cluster geometries in the size range probed here are dominated by surface atoms and deviate considerably from the bulk zinc-blende structure. To explore the relation between geometry and band splitting, we performed crude single-point energy calculations on In_9P_9 , $\text{In}_{13}\text{P}_{13}$, and $\text{In}_{20}\text{P}_{20}$ clusters with the zinc-blende structure using the B3LYP method. The clusters exhibited two bands of electronic states, with average splittings of 2.8, 3.1, and 3.6 eV for zinc-blende In_9P_9 , $\text{In}_{13}\text{P}_{13}$, $\text{In}_{20}\text{P}_{20}$ clusters, respectively. The most tightly bound states for $\text{In}_{13}\text{P}_{13}$ and $\text{In}_{20}\text{P}_{20}$ had binding energies of 8.0 and 9.1 eV, respectively. The splitting for zinc-blende In_9P_9 differs only slightly from that for the optimized structure in Fig. 2 (3.2 eV), but for zinc-blende $\text{In}_{20}\text{P}_{20}$, the calculated splitting is very close to the bulk value, suggesting that as the number of tetrahedrally coordinate atoms increases, the band spacings approach the bulk valence band splitting. This observation clearly warrants experimental verification through measurement of the PE spectra of slightly larger clusters than were considered here. Unfortunately, signal levels for larger clusters were too small to enable us to obtain their PE spectra, so this investigation will require modifications of our ion source and mass spectrometer configuration.

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