

Near-ir Absorption in Neutral Clusters of Indium Phosphide: Observation of an Optical-Gap-like Feature at 1.3–1.5 eV

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Near-ir absorption spectra are obtained for neutral InP clusters in the range 1.0–1.6 eV using two-color resonant two-photon dissociation spectroscopy. All stoichiometric and many off-stoichiometric InP clusters exhibit a distinct continuum absorption with an onset of 1.3–1.5 eV, close to the band gap of crystalline InP. Additional weaker absorptions are also seen at lower energies. An explanation is given for why these spectra are so similar to those of III-V semiconductor solids.

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Spectroscopy has been recently performed on small semiconductor clusters to probe the evolution in electronic and geometric structure with cluster size.¹⁻³ The fascinating results of these photodetachment² and photodissociation³ spectroscopic studies still do not give the desired direct optical-absorption spectra of neutral semiconductor clusters. Herein we present near-ir spectra for neutral InP clusters, obtained using two-color resonant two-photon dissociation (R2PD) spectroscopy. These are the first direct absorption spectra for small isolated neutral semiconductor clusters as a function of size. The results are surprising: Small InP clusters containing only six to twelve atoms exhibit a distinct continuum absorption with an onset close to the band gap of crystalline InP. These clusters are too small to have either bands or a bulk band gap; nonetheless, they show a continuum absorption onset, or so-called optical gap. Additional absorptions that are quite dependent on cluster size appear as weaker tails on the low-energy side of the continuum absorption. Despite their minuscule size, these clusters exhibit optical-absorption spectra which are analogous to those found in amorphous III-V semiconductor solids.

The experimental apparatus described in detail previously has been modified slightly to permit collection of two-color R2PD spectra of InP clusters.³ Clusters are produced by laser ablating bulk InP into a helium carrier gas within a supersonic expansion nozzle. The pulsed laser-ablation source assembly features a General Valve (Series 9) pulsed valve with a total nozzle length of 0.7 cm and 200-psi He backing pressure to yield a flow of 150 SCCM at 10-Hz operation (SCCM denotes cubic centimeters per minute at STP). After leaving the source, the supersonic molecular beam containing the clusters is intercepted by two spatially coincident “pump” laser pulses (colors I and II) counterpropagating along the molecular beam axis. Temporally, color I (1200–780 nm, 40 mJ/cm²/pulse) first intercepts the clusters 50 μ sec after they have exited the supersonic nozzle, followed by color II (fixed at 580 nm, 55 mJ/cm²/pulse) 20 nsec later. About 350 μ sec later, the clusters enter the ionization region of the time-of-flight mass

spectrometer where they are ionized at 7.88 eV for mass analysis. Mass spectra are recorded over the range of 425–1050 amu.

Photodissociation is used to obtain cluster-specific spectral information.³ Absorption and dissociation events are separated by using two different color photons to accomplish R2PD. The first color I photon performs the spectroscopy and the second, higher-energy, color II photon adds additional energy in order to produce the detectable dissociation events. This absorption is detected by a depletion of the signal corresponding to the absorbing clusters in the mass spectrum since the dissociation fragments recoil from the narrowly defined molecular beam. Although two-color R2PD is much more difficult to implement than simple one-color photodissociation, it is necessary for monitoring the near-ir absorptions of many InP clusters. Stoichiometric clusters in particular are especially stable and do not exhibit single-photon photodissociation at energies below 1.5 eV.³

A photon energy of 2.1 eV is selected for color II. This gives a combined energy for colors I and II that is sufficient to readily dissociate even a relatively stable cluster without dissociating most of the clusters with color II alone. At 2.1 eV, all of the clusters studied are also observed to have a strong electronic resonant absorption.³ Lifetime measurements show that rapid internal conversion occurs following absorption of color I; therefore, absorption of the second photon, color II, occurs independently. We record and independently average mass spectra for each of the four combinations: colors I and II on, color I only on, color II only on, neither color I nor II on. Each combination is repeated every four cluster pulses to minimize contributions from fluctuations in the cluster source. Mass spectra are averaged for 6000 complete sequences at a net repetition rate of 2.5 Hz.

The success of the two-color R2PD technique in obtaining near-ir cluster spectra is illustrated in Fig. 1. Figure 1(a) shows the near-ir spectrum of In₄P₂ obtained using one-color photodissociation. The In₄P₂ mass peak

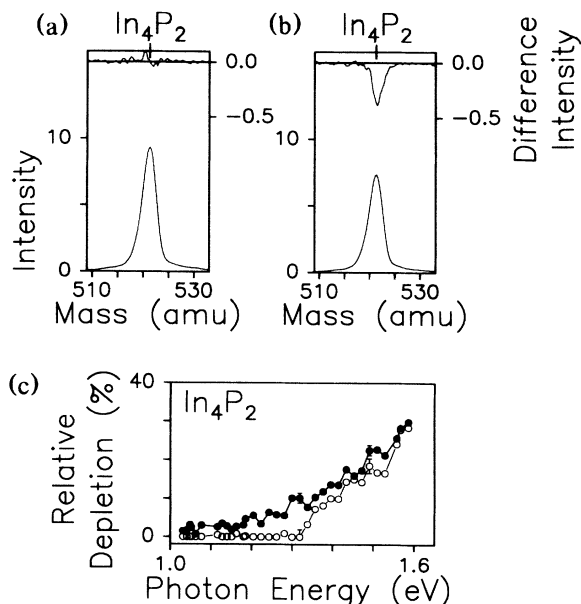


FIG. 1. One-color and two-color resonant photodissociation of In_4P_2 . Color I, 1.25 eV; color II, 2.1 eV. (a) Under single-color conditions (color II off), recorded mass spectrum (color I off) and difference mass spectrum (color I on - color I off). (b) Under two-color conditions (color II on), recorded mass spectrum (color I off) and difference (color I on - color I off) spectrum. (c) Spectral dependences of In_4P_2 depletion signal under one-color (○) and two-color (●) (color II fixed at 2.1 eV) conditions. Representative error bars are given at 1.32 and 1.49 eV.

intensity is the same whether color I is on or off. Irradiation with both color I and color II photons, however, causes significant depletion to the In_4P_2 peak, Fig. 1(b). The spectral dependence of the one-color versus two-color depletion behavior of In_4P_2 is apparent in Fig. 1(c). Note that the two-color R2PD technique clearly shows that these clusters are absorbing far below the ~ 1.3 -eV "threshold" of the single-photon data. Well above this photodissociation threshold energy, the one- and two-photon-dissociation absorption dependences are in excellent agreement. The location of this "threshold energy" is given by the dissociation energy and internal temperature of the cluster. Using InP-cluster dissociation energies determined previously, we estimate the internal InP-cluster temperature to be 500 K under the present source conditions.³ We have previously determined the single-photon absorption cross sections to be $(2-5) \times 10^{-18} \text{ cm}^2$.³ From the data in Fig. 1(c), we estimate that the cross sections for absorption of the color I photons are of similar magnitude.

Complete two-color R2PD spectra are given in Fig. 2 for all of the stoichiometric, $(\text{InP})_x$, clusters that we were able to access, In_3P_3 - In_6P_6 . The spectra that we were able to obtain for clusters which differ from equal stoichiometry by a single P or In atom are shown in Fig.

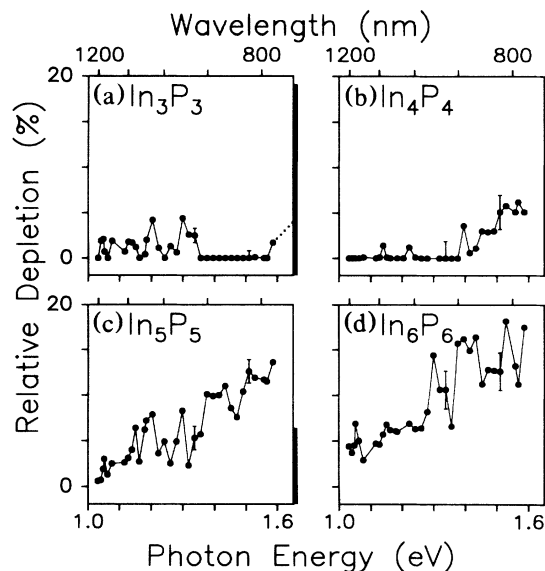


FIG. 2. R2PD spectra of the stoichiometrically even clusters In_3P_3 - In_6P_6 as a function of color I frequency. Color II is fixed at 2.1 eV. Data points (●) are connected by straight lines. The dashed line for In_3P_3 (a) indicates observed absorption behavior measured at higher photon energies (Ref. 3). The solid bar immediately to the right of each plot represents the relative intensity of each of the clusters in a mass spectrum recorded with neither color I nor color II on. Representative error bars are given at 1.34 and 1.51 eV. For comparison, the bulk band gap of InP is 1.18 eV (500 K).

3. To our knowledge, these are the first absorption spectra to be recorded for small semiconductor clusters containing more than 2-3 atoms.

The most striking trend in the stoichiometric cluster spectra is the onset of a strong continuumlike absorption at the blue end of the spectra which shifts slowly to lower energies with increasing cluster size. For In_3P_3 , it begins at ~ 1.56 eV, shifting to ~ 1.4 eV for In_4P_4 , ~ 1.3 eV for In_5P_5 (this is less obvious), and then ~ 1.25 eV for In_6P_6 . In contrast, features which appear at lower energy in the spectrum between about 1.0 and 1.3 eV vary with cluster size. The In_3P_3 spectrum shows considerable structure between 1.0 and 1.3 eV, followed by a distinct null before the continuumlike absorption onset. In_4P_4 appears to have no lower-energy absorptions [given the small abundance of In_4P_4 , the weaker absorption peaks at ~ 1.1 and ~ 1.2 eV in Fig. 2(b) are probably not real]. Note that the absorption nulls in the In_3P_3 and In_4P_4 spectra may be missing for In_5P_5 and In_6P_6 simply because the higher-energy features have moved to lower energy and merged with the lower-energy absorptions.

Addition of either a P or an In atom to the cluster causes a major change to the cluster spectra, Fig. 3. Nonetheless, the onset of a continuum absorption can be seen clearly in the off-stoichiometric clusters In_4P_3 and In_5P_4 . In general, the spectra for these off-stoichiometric clusters show more intense absorptions throughout this

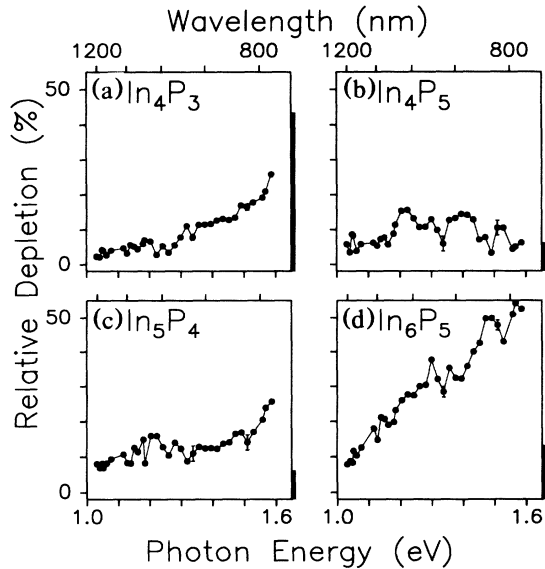


FIG. 3. As in Fig. 2; absorption spectra of several $\text{In}_x\text{P}_{x\pm 1}$ stoichiometrically uneven clusters.

spectral range than those for the corresponding stoichiometric clusters.

These InP-cluster absorption spectra show the first direct evidence of electronic states below the bulk band gap ($E_{\text{gap}} = 1.18$ eV at 500 K) and an optical-gap-like feature near the bulk band gap for semiconductor clusters both in this size regime and in the nanometer-size regime.^{2,4} Low-energy transitions are not surprising for the off-stoichiometric clusters, which have been observed to have strong absorptions that start as low as 0.6 eV and extend well into the visible.³ Given their odd number of valence electrons, the off-stoichiometric clusters must be open-shell systems with many low-lying excited states. Despite the optical absorptions of the stoichiometric clusters at these low energies, several independent pieces of experimental evidence suggest that they are closed-shell singlets. All of them exhibit higher ionization potentials than similar size clusters with an odd number of atoms,^{1(b),3} and several of them (In_3P_3 and In_5P_5) are particularly stable with respect to dissociation.³ The most compelling comparison is between the many spectra that we have obtained for odd-numbered clusters (e.g., Fig. 3) versus even-numbered clusters, both stoichiometric and nonstoichiometric [e.g., Figs. 1(c) and 2]. With few exceptions, the spectra for the even-numbered clusters are more structured, less intense, and have weaker absorptions below roughly 1.4 eV. In contrast, the odd-numbered clusters exhibit stronger absorptions that typically are quite significant even at 1.0 eV and rise rather smoothly with increasing energy.

The absorption continuum spectral feature exhibited by small InP clusters bears an amazing similarity to bulk InP. This continuum feature persists for these clusters quite independent of size and, in most cases, stoichio-

metry. In the larger clusters, the onset of this feature lies just above the crystalline InP bulk band gap at 1.18 eV (500 K). We propose that this transition in small InP clusters is related to the bulk band-gap transition. The optical absorption at the band gap in the solid is well known to be governed by electrons in In-P bonding orbitals.⁵⁻⁷ Small InP clusters must surely have In-P bonds. By analogy to the bulk band-gap transition, we propose that the absorption continuum feature in the cluster spectra arises from a $\sigma\text{-}\sigma^*$ transition involving the cluster In-P bonding orbitals. Furthermore, we suggest that the energy of this transition is similar to that in the bulk because the clusters have some In-P bonding orbitals with much the same p -like character and energetics as those just above and below the gap in the bulk.

Most of the InP-cluster spectra also exhibit weaker absorption features to the red of the continuum absorption. We propose several possible explanations for these transitions, based on some of the types of structural deviations known to produce states in the gap for bulk III-V semiconductors.⁶⁻⁸ States are created in the gap by dangling bonds at the surface, cation-cation (e.g., In-In) "wrong bonds," and other antisite or vacancy defects. Given the severe coordinative unsaturation in these small InP clusters, any of these analogous situations is possible. The number of any such dangling bonds, In-In bonds, etc., would be expected to vary considerably with cluster size, structure, and isomeric form. This would account for why the weaker absorptions are observed to vary strongly with cluster size and stoichiometry.

No theoretical calculations have been performed on any of the InP clusters in our study. Preliminary theoretical results are available, however, for two chemically analogous clusters, Al_3P_3 and Ga_5As_5 .^{9,10} All of the two- and three-dimensional forms that have been calculated to be stable minima for these clusters deviate markedly from microcrystalline fragments of the zincblende structure of bulk III-V semiconductors. Thus far, these calculated structures indicate that small III-V clusters are nonmetallic, and have strongly directional, covalent bonds, including numerous III-V bonds. Further theoretical calculations will be necessary to investigate the nature of the cluster bonding orbitals and resulting electronic states.

The band-gap-like absorption with a varying tail to lower energy exhibited by these small InP clusters is remarkably similar to the optical behavior observed in amorphous III-V semiconductors.⁷ Optical properties of amorphous III-V materials have been rationalized by bond-angle fluctuations, wrong bonds (III-III and V-V bonds), odd membered rings, antisite defects, etc. The relative contribution of these various types of chemical disorder in these materials is still unresolved. Furthermore, some of these theoretical models are difficult to reconcile with spectroscopic probes of amorphous III-V semiconductor local structure.⁷ Given that the preparation methods for these materials favor disorder, more

profound forms of chemical disorder have been proposed but virtually nothing is known about the properties of such structures. The small InP clusters that we have studied present an opportunity to study the properties of semiconductors which differ radically on the atomic scale from the structures of bulk compounds. Understanding why these small InP clusters have an optical signature so similar to that in the bulk will provide a means of exploring the electronic contributions of analogous types of disorder in amorphous semiconductors.

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