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Theoretical Investigation of the Influence of Ligands on Structural and Electronic Properties of Indium Phosphide Clusters

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Results of a theoretical study of the effects of including ligands on stoichiometric In_nP_n clusters are presented. We apply a parametrized density-functional method and consider clusters with n up to above 70. As ligands we consider H atoms and CH_3 groups, and the results are compared with our earlier ones for the naked clusters. We find that the ligands lead to only smaller structural changes but that an enhanced In-to-P electron transfer in the outermost parts of the clusters, which we observed for the naked clusters, is largely suppressed, so that there is a more homogeneous In-to-P transfer throughout the whole cluster. Adding the ligands leads, in most cases, to an increase in the HOMO−LUMO gap and, therefore, also to an increase in the stability of the clusters. However, we find also that the HOMO−LUMO gap depends critically on the type, sites, and number of ligands that are added.

I. Introduction

During the past few years semiconductor nanomaterials have been acquiring much interest both in basic research and in applied science. This can be attributed to two effects. First, the reduced dimensions lead to quantum-confinement effects,[1−5] and second, the large number of surface atoms compared with the total number of atoms leads to a high chemical reactivity of such materials. The quantum-confinement effects become important when, e.g., the spatial extension of an exciton becomes comparable with the size of the nanoparticle, in which case it may be possible to tune the electronic and optical properties through size variation. On the other hand, the fact that a naked semiconductor nanoparticle has a large surface with many dangling bonds leads to a number of chemically active orbitals close to the Fermi level. Saturating those with ligands may, accordingly, increase the stability of the material, remove orbitals from the vicinity of the Fermi level, and, accordingly, modify the optical, electronic, and structural properties of the nanoparticles.

As an extension of our earlier work[6] where we studied theoretically naked InP nanoparticles, here we present results for such clusters where CH_3 groups or H atoms have been used in passivating the dangling bonds. We shall thereby explicitly focus on the effects of the ligands on the optical, electronic, and structural properties.

A number of experimental and theoretical studies of the properties of nanomaterials, including both metals and semiconductors, has been presented (see, e.g., ref 7). However, experimental and theoretical studies often consider different systems. Thus, most of the experimental studies are performed in solution, and the clusters are stabilized by surfactants/ligands. Theoretical studies, however, can mimic the experimental setup only partly, so that these most often consider naked, isolated clusters in the gas phase. Theoretical studies on passivated semiconductor clusters are scarce. To date, maximum attention on clusters with surfactants has been given to passivated silicon nanostructures such as clusters, wires, and slabs[8−13] and to carbon nanostructures.[14] That the surfactants can have significant effects on the material properties was shown, e.g., for Si clusters where they changed the energy gap separating the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) from essentially 0 to 3.4 eV.[15] Moreover, as shown by Draeger et al.[16,17] not only the number but also the type of the ligands can affect the optical properties of the nanoparticles drastically.

In our previous study[6] on stoichiometric ($n = m$) and nonstoichiometric ($n \neq m$) In_nP_m clusters we considered structures that were derived from zinc blende and wurtzite crystal structures by cutting out a spherical part and, subsequently, letting that relax to the closest total-energy minimum. The stoichiometric clusters were obtained by placing the center at the midpoint of an In−P nearest-neighbor bond, whereas for the nonstoichiometric clusters the center was put at an atom. In the present work we consider only the stoichiometric clusters but proceed otherwise as above except that we have added ligands to the surface. In experimental studies one often uses large ligands such as trioctylphosphineoxide (TOPO),[18] but for several reasons we chose here to consider smaller ones such as methyl groups or hydrogen atoms. First, the computations become considerably simpler when using the smaller ligands. Second, for the larger ligands steric effects may reduce the number of ligands that can be added to a given cluster, whereas with the smaller ligands we can study how the properties change when gradually changing the number of ligands. Third, by choosing hydrogen atoms or methyl groups as ligands we expect that we first are saturating dangling bonds, whereas for more electronegative or -positive ligands we may include additional effects due to charge transfers that are beyond the scope of the present work. Fourth, by considering the same structures as in our previous work we are able to identify the effects of the ligands most clearly. We will show that the results for those two ligands are similar, making us propose that this also would be the case when considering other ligands as long as charge transfers between the cluster and the ligands are minimal. We add, however, that the lack of precise experimental information

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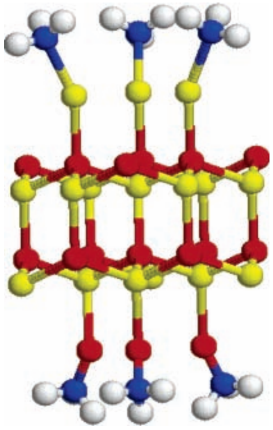

Figure 1. Initial structure for the zinc blende-derived cluster with 16 pairs of InP and passivated with 6 methyl groups.

on the structure of larger clusters may be a source of disagreement between our results and those from experiment.

The site selection for passivation remains one of the problems for theoretical calculations. Eichkorn and Ahlrichs added ligands to CdSe clusters so that all Cd and Se atoms were 4-fold coordinated.[19] However, experimental studies on surface-passivated InP nanocrystals[20] have indicated that at least for larger nanocrystals only part of the surface sites has been saturated. Moreover, from the work of Joswig et al.[21] on cadmium sulfide clusters it is evident that the single-bonded atoms are those surface atoms that give rise to orbitals in the vicinity of the Fermi level. Therefore, we choose to passivate only the single-bonded surface atoms. In addition, this makes the calculations computationally more efficient and enables us to investigate larger clusters as well. As an example we show in Figure 1 the initial structure for a zinc blende-derived cluster with 16 pairs of InP, including 6 single-bonded surface atoms to which 6 methyl groups have been added. The paper is organized as follows. In the subsequent section we describe the computational method used for the calculation. This section is followed by the results that are divided into two parts, of which one part is devoted to structural properties and the other to the electronic properties, i.e., Mulliken populations, the frontier orbitals, the density of states, and the dependence of the optical gap on the cluster size. Finally, the last section summarizes our findings.

II. Computational Method

We have used a parametrized density-functional tight-binding method that has been described in detail elsewhere.[22−24] According to this method the binding energy of a given system is written as

$$E_{\mathrm{b}} = \sum_i \epsilon_i - \sum_{jk} \epsilon_{jk} + \frac{1}{2}\sum_{k\neq l} U_{kl}(|\vec{R}_k - \vec{R}_l|) \qquad (1)$$

Here, ϵ_i is the energy of the ith orbital for the system of interest and ϵ_{jk} is the energy of the jth orbital for the isolated kth atom. Finally, U_{kl} is a pair potential between the kth and lth atom. The valence single-particle eigenfunctions $\psi_i(\vec{r})$ to the Kohn−Sham equations $\hat{h}\psi_i = \epsilon_i\psi_i$ are expanded in a set of atom-centered basis functions $\chi_{klm}(\vec{r})$. Here, k denotes the atom and (l, m) the angular dependence. The matrix elements $\langle\chi_{k1l1m1}|\hat{h}|\chi_{k2l2m2}\rangle$ and $\langle\chi_{k1l1m1}|\chi_{k2l2m2}\rangle$ are obtained from density-functional calculations on the diatomic molecules. Finally, the pair potentials U_{kl} are determined so that the binding-energy curves of the diatomics are reproduced accurately. Only In 5s and 5p, P 3s and 3p, C 2s and 2p, and H 1s electrons were explicitly included in the calculations. Although it can be argued that In 4d electrons should also be treated explicitly, we did not do so. For the isolated atom these orbitals lie about 5 eV below the P 3s orbitals, and moreover, their effects are indirectly included in the potentials U_{kl}. It shall be mentioned that our approach is nonself-consistent, which may cause some inaccuracies in the relative positions of the orbital energies. We emphasize, however, that in the present study we focus on the properties of the InP part of the nanoparticles and, therefore, that in particular those parts of the parametrized method that describe In and P should be accurate. In our earlier work we argued that this indeed was the case.[6]

III. Results and Discussion

A. Structural Properties.

In the first subsection we will discuss the structural properties of the passivated clusters and thereby focus on the In and P atoms and, moreover, compare unrelaxed and relaxed clusters as well as clusters without ligands and clusters with H atoms or CH_3 groups as ligands. The initial, unrelaxed structures are finite, spherical parts of the zinc blende or wurtzite crystal structures with the center at an In−P nearest-neighbor bond. To analyze the structure we first define the center of the In_nP_m cluster through

$$\vec{R}_0 = \frac{1}{n+m}\sum_{j=1}^{n+m}\vec{R}_j \qquad (2)$$

and, subsequently, for each atom its so-called radial distance

$$r_{\mathrm{j}} = |\vec{R}_j - \vec{R}_0|, j = 1, 2,..., n + m \qquad (3)$$

For the naked clusters we found previously[6,25−27] that analyzing the radial distances of the atoms provided useful information on structural relaxations that, moreover, were found to be largely confined to a layer of 2.5−3 Å thickness. To study how the presence of the ligands affect this, we show in Figure 2 the number of In and P atoms with a certain radial distance as a function of this distance for different clusters. In all cases the radial distance of the unrelaxed cluster is, of course, independent of the presence and type of ligands. In general, we see that most often the larger structural relaxations are confined to the outer parts of the clusters, which should not be a surprise. Moreover, as we found for the naked cluster,[6,25−27] In and P atoms in the outer parts behave differently with the In atoms preferring to move toward the center of the cluster, giving them a larger coordination, whereas the P atoms more often are the outermost atoms (i.e., those with the largest radial distances). Finally, with only minor modifications we find that the H and CH_3 ligands lead to very similar structures that in turn differ very little from the structures of the unpassivated systems.

B. Electronic Properties.

Further information about the differences for clusters without and with ligands can be extracted from Figure 3, which shows the Mulliken gross populations for the In and P atoms as functions of the radial distance. Here, only the valence electrons are considered, i.e., three for neutral In and five for neutral P atoms. Since the In and P atoms have different populations, this figure clearly demonstrates the consensus from the previous

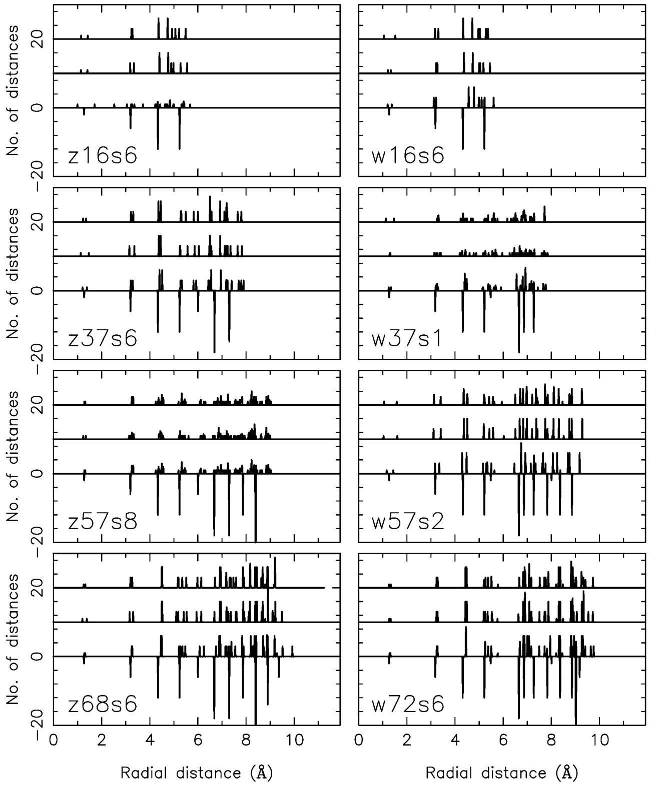

Figure 2. Radial distribution (i.e., number of atoms with a given radial distance) of indium and phosphorus atoms for zinc blende- (left column) and wurtzite-derived clusters (right column) of different sizes and with different types of ligands. In each panel the curve pointing downward gives the distribution for the unrelaxed cluster whereas the curves pointing upward give the distribution for (from below) the relaxed cluster with methyl groups, the relaxed naked cluster, and the relaxed cluster with hydrogen atoms. The labels in the panels z37s6 and w37s1 indicate zinc blende- (z) or wurtzite- (w) derived clusters with 37 InP pairs and 6 (first example) or 1 (second example) ligands.

subsection, i.e., that the outermost atoms are P atoms. Comparing the clusters without and with ligands we also see that in the inner part of the cluster there is essentially no difference. However, charge transfer is enhanced in the surface region, more for the unpassivated clusters than for the passivated ones, and in fact, we previously used this in defining a surface region for the naked clusters.[6,25,28] The effect of the ligands is, first, to reduce this transfer in the surface region with the atoms to which the ligands are bonded being those that experience the largest reductions. We add that the figure does not display the results for the H-passivated clusters that, however, differ only marginally from those of the methyl-passivated clusters.

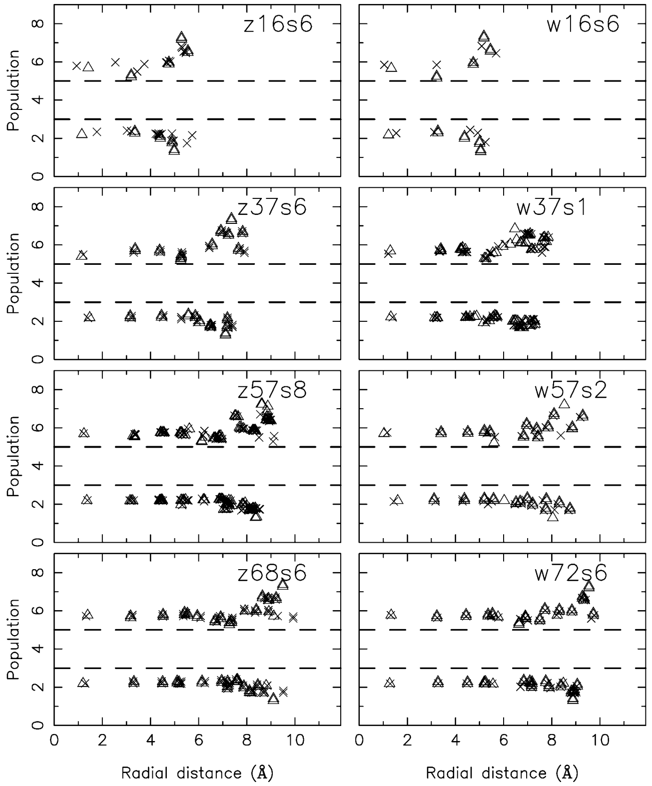

Figure 3. Mulliken gross populations for the valence electrons of indium and phosphorus atoms as a function of the radial distance for the same (relaxed) structures as in Figure 2. The horizontal dashed lines mark the values for the neutral atoms, i.e., 3 for In and 5 for P. The crosses show the results for the clusters with methyl ligands, whereas the triangles show the results for the naked clusters. For the sake of simplicity, we do not show the results for the H-passivated clusters. The notation used for the labels is the same as that used in Figure 2.

The optoelectrical properties of semiconductor nanoparticles are dominated by excitonic effects, in particular by the recombination of the electron−hole pairs forming the excitons. To a first approximation the excitonic wave function is determined by the orbitals closest to the gap, i.e., the HOMO and LUMO, and the relaxation processes will, therefore, depend strongly on the spatial distribution of these orbitals. Here, we will analyze the latter in detail. The fact that our approach suffers from two deficits that may affect the band gap in opposite directions, i.e., a density-functional approach will usually give too small band gaps whereas the use of a minimal basis set may lead to too large band gaps, may be relevant for the absolute value of the optical band gap, but, we believe, less important when analyzing the spatial distribution of the frontier orbitals or the size dependence of the optical properties. Therefore, to study the spatial distribution of the orbitals we proceed as follows.

For any orbital we construct the density

$$\rho_i(\vec{r}) = \sum_j N_{ij}\left(\frac{2\alpha}{\pi}\right)^{3/2}\exp[-\alpha(\vec{r} - \vec{R}_j)^2] \qquad (4)$$

Here, N_{ij} is the Mulliken gross population for the jth atom and ith orbital and α is a fixed constant. Subsequently, we calculate (and depict) the spherical average of this density about the center of the cluster. Since we are interested in a qualitative and comparative description of the radial distribution of the orbitals, we choose a fixed value of α for all orbitals and atoms instead of analyzing the true density of each orbital. The value of α is chosen so that illustrative figures result.

This radial dependence of the HOMO and LUMO is shown in Figure 4 for both methyl-passivated and naked clusters. It is clearly seen that passivation does affect the orbitals somewhat. In this context it should be remembered that, as shown, e.g., in Figure 2, the passivated clusters are, in general, spatially more extended than the naked ones, so that the results of Figure 4 imply that the frontier orbitals are not centered on the outermost atoms. Instead, the HOMO and LUMO have very small contributions from those atoms to which the ligands are attached.

Figure 5 shows the total density of states (slightly broadened by Gaussians) for a few selected clusters with either hydrogen atoms or methyl groups as ligands in comparison with that of the naked clusters. The four panels are very similar. In all cases

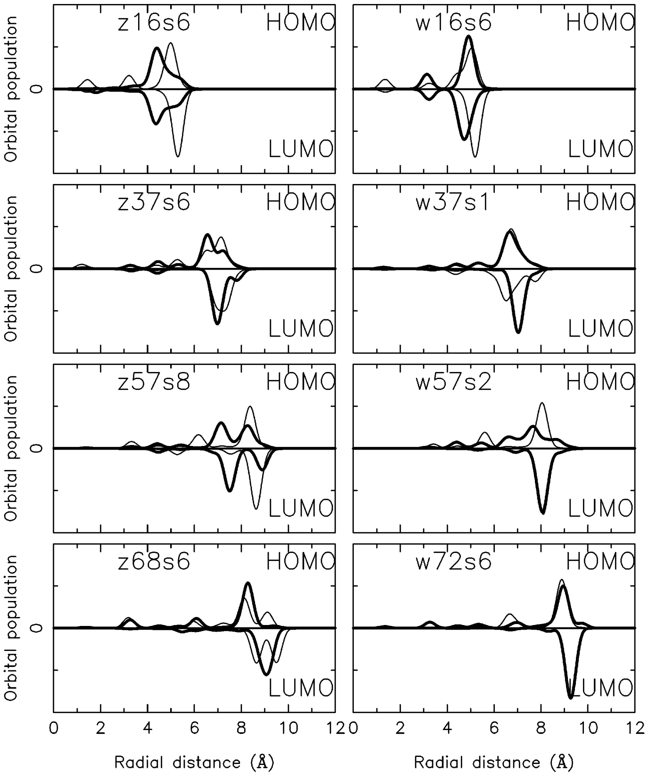

Figure 4. Schematic representation of the radial distribution of the HOMO and LUMO for the same relaxed methyl-passivated and naked clusters as in Figure 2. The upper (lower) part of each panel represents the HOMO (LUMO). The thick (thin) curves show the results for the methyl-passivated (naked) clusters. The notation used for the labels is the same as that used in Figure 2.

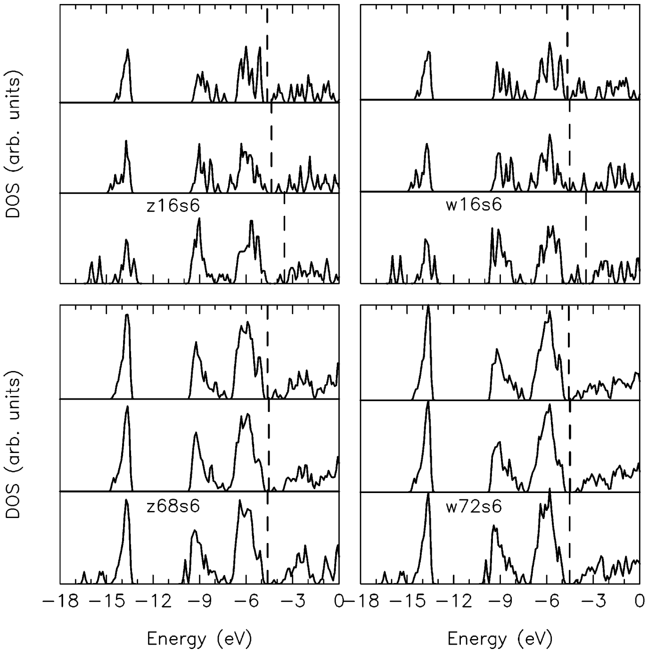

Figure 5. Density of states (DOS) for different zinc blende- (left column) and wurtzite-derived (right column) clusters of different sizes. The vertical dashed lines mark the Fermi energy. In each panel the bottom, middle, and top curve shows the results for the CH_3-passivated, H-passivated, and naked cluster, respectively. The notation used for the labels is the same as that used in Figure 2.

the methyl-passivated clusters have some deep-lying orbitals below roughly −16 eV that are lacking in the other cases. In all other cases we have orbitals in the range from −15 to −13 eV mainly due to 3s functions of P atoms, whereas those above −10 eV are due to In 5s and 5p functions together with P 3p functions. The low-lying orbitals for the methyl-passivated clusters might interact with In 4d orbitals if those were explicitly included in the calculations. We expect, however, that including these would lead to only minor changes in our conclusions.

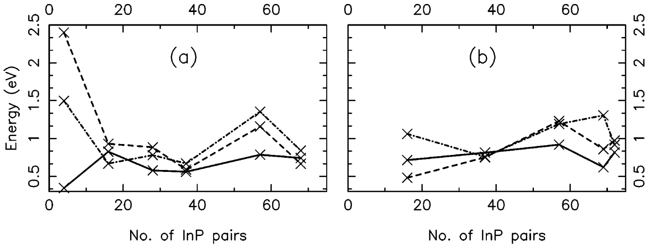

Figure 6. HOMO−LUMO gap vs cluster size for (left) zinc blende- and (right) wurtzite-derived clusters. The solid curve shows the gap for naked clusters, the dashed curve shows those for hydrogen-passivated clusters, and the dash−dotted curve shows those for methyl-passivated clusters.

A careful examination of Figure 5 shows that the HOMO−LUMO gap depends significantly on both the size of the cluster (as found in our earlier studies on various AB semiconductor clusters[28]) and the ligand. Since this HOMO−LUMO gap is essential for the optical properties of those systems, we will study this in more detail.

First, in Figure 6 we show this gap as a function of the size of cluster for both for naked and passivated clusters. It is seen that in most cases (with the smallest clusters in some cases being exceptions) the naked clusters are those with the smallest gap, in accordance with the observation that the frontier orbitals for those are localized to the outermost atoms that, in turn, contain unsaturated bonds, so that saturating those should lead to increases in the HOMO−LUMO gap, neglecting all other effects. Moreover, we see that the passivated clusters show some differences depending on whether the ligands are H atoms or CH_3 groups. The fact that the HOMO−LUMO gap is larger for the clusters than for the bulk value (1.34 eV) is in good agreement with the results of Neumark et al. on naked clusters,[29,30] although the issues related to our calculated band gaps that were mentioned above remain valid.

Another observation from our earlier studies on naked CdS, CdSe, InP, and ZnO clusters[28] is that there is a close correlation between the HOMO−LUMO energy gap and the stability of the clusters. This can be interpreted as a special case of the well-known HSAB (hard and soft acids and bases) principle.[31] This correlation remains partly for the passivated clusters, since, according to our calculations, those clusters for which the HOMO−LUMO gap in the unpassivated case was large, also when being passivated have a large gap.

Finally, in Figure 7 we show that the optical properties depend critically on where the ligands are placed on the clusters, how many are put there, and the type of the ligands. In this figure we are considering the cluster with the most single-bonded atoms, i.e., the zinc blende-derived $In_{28}P_{28}$ cluster for which there are six single-bonded P and six single-bonded In atoms. Whenever an odd number of ligands is attached, the total number of electrons is odd and, accordingly, one orbital is only singly occupied. The figure shows that the energetically lowest orbital that remains unoccupied in all cases has an energy that is largely independent of the ligands. The same is to a much lesser extent true for the energetically highest orbital that remains occupied in all cases. This orbital as well as the one that is partly occupied show some dependence on the presence, number, type, and position of the ligands.

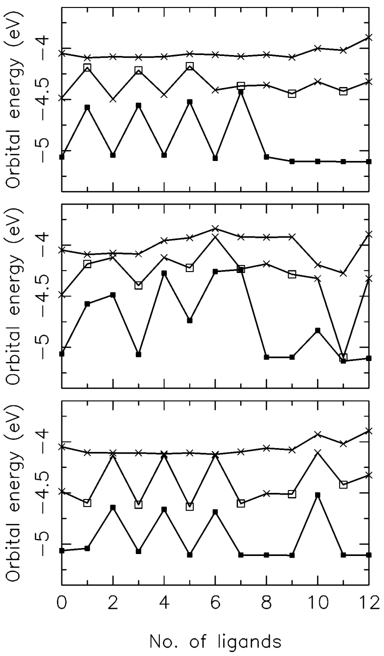

Figure 7. Energies of the orbitals closest to the Fermi level for the zinc blende-derived $In_{28}P_{28}$ cluster as a function of the number of methyl groups or hydrogen atoms attached to it. The closed and open squares as well as crosses mark orbitals that are doubly and singly occupied as well as empty, respectively. In the upper panel methyl groups have been added alternating In and P atoms, whereas in the two lower panels hydrogen atoms have been added either (middle panel) first to the six outermost In atoms and subsequently to the six outermost P atoms or (lower panel) vice versa.

IV. Conclusions

Experimentally produced InP nanoparticles are only rarely naked but are either passivated and stabilized through ligands on the surface or, e.g., as quantum dots, embedded in a crystalline matrix. On the other hand, theoretical studies often consider idealized structures where, in particular, ligands often are either completely neglected or included in an idealized way. The effects of the ligands may, however, be profound, and therefore, in the present study we examined their role in detail. We studied stoichiometric In_nP_n clusters whose structure was derived from the crystalline wurtzite or zinc blende structure and compared the structural and electronic properties of naked clusters with those of clusters with H atoms or CH_3 groups as passivating ligands. Our choice of ligands was motivated by more issues: the small size made the computations simpler and, thereby, allowed for more systematic studies; we expect that these ligands will mainly saturate dangling bonds without leading to significant charge transfers; and, finally, we could systematically study how the properties change when adding more and more ligands without being disturbed by steric effects. The latter is facilitated by considering the same structures as in our previous work on naked InP clusters. On the other hand, we cannot exclude that other ligands such as TOPO will modify the conclusions we found here, first to charge-transfer effects.

We found that the presence of the ligands leads to only minor structural changes. Not surprising, most changes occur—independent of the presence of the ligands—in the outermost parts of the clusters. On the other hand, the Mulliken gross populations show that the enhanced In-to-P electron transfer, which is found for the naked clusters in the outer parts of the clusters, is largely suppressed when adding ligands to the clusters. Nevertheless, also in this case the In atoms donate electrons to the P atoms.

On the basis of this finding one may suggest that the HOMO has dominating contributions from the outermost P atoms and the LUMO from the outermost In atoms. This is, however, not found; rather the contrary occurs. Accordingly, the orbitals on the P atoms where the donated electrons enter must appear at energies somewhat (maybe only slightly) below that of the HOMO, and similarly, In-derived orbitals that have become emptied upon electron transfer to P must appear at energies above that of the LUMO.

We found that in most cases the ligands led to an increase in the HOMO−LUMO gap, which can be interpreted as an indication of larger stability. However, as we showed for $In_{28}P_{28}$, the energy gap may depend critically on sites, types, and number of the ligands.

In total our study suggests that the role of the ligands on the structural properties of the nanoparticles is more limited than what one may expect when choosing ligands for which only a minor charge transfer takes place. This does, however, not indicate that they, in experimental studies, can be eliminated: they may be important in order to avoid chemical reactions between the nanoparticles and other parts of the system of the experimental studies: one has to remember that in most cases these nanoparticles are less stable than the crystalline materials. Furthermore, the presence of the ligands leads to noticeable changes in the electronic properties of the nanoparticles.

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