Electronic Structure Origins of Surface-Dependent Growth in III-V Quantum Dots

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ABSTRACT: Indium phosphide quantum dots (QDs) have emerged as a primary candidate to replace more toxic II-VI CdSe QDs, but production of high-quality III-V InP QDs with targeted properties requires a better understanding of their growth. We develop a first-principles-derived model that unifies InP QD formation from isolated precursor and early stage cluster reactions to 1.3-nm magic size clusters, and we rationalize experimentally-observed properties of full sized > 3 nm QDs. Our first-principles study on realistic QD models reveals large surface-dependent reactivity for all elementary growth process steps including In-ligand bond cleavage and P precursor addition. These thermodynamic trends correlate well to kinetic properties at all stages of growth, indicating the presence of labile and stable spots on cluster and QD surfaces. Correlation of electronic or geometric properties to energetics identifies surprising sources for these variations: short In…In separation on the surface produces the most reactive sites, at odds with conventional understanding of strain (i.e., separation) in bulk metallic surfaces increasing reactivity and models for ionic II-VI QD growth. These differences are rationalized by the covalent, directional nature of bonding in III-V QDs and explained by bond order metrics derived directly from the In-O bond density. The unique constraints of carboxylate and P precursor bonding to In atoms rationalizes why all sizes of InP clusters and QDs are In-rich but become less so as QDs mature. These observations support the development of alternate growth recipes that take into account strong surface-dependence of kinetics as well as the shapes of both In and P precursors to control both kinetics and surface morphology in III-V QDs.
1. Introduction

The unique size-dependent electronic and optical properties\(^1\) of colloidal quantum dots (QDs) make them ideal for applications in photovoltaics,\(^3\) light-emitting diodes,\(^6\) and biological imaging.\(^8\) Although II-VI CdSe QDs exhibit controllable sizes\(^10\) and light emission throughout the visible range\(^12\), III-V InP QDs have emerged as a less toxic\(^13\) alternative\(^14\) with even broader emission range.\(^16\) Adoption of InP QDs has been limited by difficulties\(^14\) in obtaining optimally narrow QD size distributions and high photoluminescent quantum yields, despite ongoing experimental efforts to understand the QD formation mechanism\(^18\) and tune the growth process.\(^24\) The typical InP synthesis recipe requires high temperatures, employs indium carboxylates\(^26\) that necessitate reactive phosphorus precursors, and long reaction times, making control of size distributions challenging.\(^29\)

Classical nucleation theory (CNT)\(^30\) has been an effective guide for tuning size distributions in more ionic II-VI and IV-VI\(^10\), QDs but nonclassical (i.e., multi-step) nucleation and growth models are needed\(^33\) to understand III-V materials.\(^19\) For example, reducing the reactivity of P precursors in accordance with CNT\(^24\) did not improve InP QD size distributions.\(^33\) InP magic size clusters (MSCs)\(^19\) around 1.1\(^42\) to 1.3\(^42\) nm in size have been observed to be essential intermediates during InP growth, with their size\(^42\) and stability\(^19\) controlled by In precursor chemistry. InP MSCs have been used as seeds for controlled QD growth\(^19\) by decoupling the nucleation and growth stages\(^21\). Although MSCs appear an essential key to understanding III-V InP\(^19\), and InAs\(^44\) growth mechanisms, controlled growth of MSCs has also been observed to be beneficial in II-VI materials (e.g., CdS\(^45\), CdTe\(^46\), and ternary II-VI alloys\(^47\)). Indeed, there is increasing consensus that small clusters and MSCs coexist with QDs during growth for a number of materials.\(^19\) The mechanism by which InP QDs form
from MSCs remains an open question, with agglomeration unlikely but either dissolution or continued growth at a slower rate both possible.\(^{34}\)

In light of a complex and challenging growth process, precursor variation\(^{19,49-50}\) during synthesis\(^{51-54}\) or post-synthetic ligand exchange\(^{55-58}\) on MSCs and QDs have been vigorously pursued experimentally. These efforts have led to discovery of alternate chemistries that can produce unique QD shapes\(^{51,55}\), size\(^{14,49}\), stability\(^{19}\), stoichiometry\(^{56-57}\), and quantum yield\(^{52-53}\), especially through apparent improvements in non-In-passivated surface properties.\(^{54,58-59}\) However, a nanoscale understanding of the QD structure during stages of growth has only been possible in a few cases\(^{43,48}\). First-principles simulations have been a valuable complement in understanding the growth mechanism\(^{60-61}\) of II-VI and IV-VI QDs. Although properties of amorphous\(^{62}\), bulk\(^{63-65}\), and quantum-confined InP\(^{62,66-69}\) had been studied in detail, our recent combined \textit{ab initio} molecular dynamics (AIMD) and reaction pathway analysis approach represented the first attempt to discover the growth kinetics and character of early stage intermediates in InP QD synthesis.\(^{70}\) Through AIMD, we observed\(^{70}\) the formation of the earliest stage clusters (ESCs) from isolated precursors in InP QD synthesis. This ESC\(^{70}\) has an indium rich surface surrounding an In\(_4\)P tetrahedron with bond lengths and surface carboxylate coordination properties in fortuitously good agreement with simultaneously obtained X-ray crystal structures of InP magic sized clusters\(^{19,34,43}\). We also confirmed the paramount importance of In precursors in controlling growth\(^{70}\), and we identified ligand modifications that could provide pathways for low-temperature synthesis\(^{71}\).

In order to continue to move beyond the limits of CNT, first-principles simulation will provide needed insight to reveal commonalities and variations in the surface chemistry of first-principles ESCs and the experimental MSC structure in order to understand how reactivity
changes during QD growth. In this work, we develop a unified electronic structure interpretation of surface reactivity on early-stage\textsuperscript{70} and magic sized\textsuperscript{43} clusters. We identify high variability of surface site kinetic and thermodynamic properties that depend strongly on nearest neighbor In-In distances in an unexpected manner but can be rationalized through the highly covalent electronic structure at the InP QD surface. This strong relationship between structure and energetics also permits us to interpret and rationalize relative quantities of excess In on the surface of experimentally-characterized\textsuperscript{48} 3 nm QDs. In Section 2, we summarize the systems selected and properties studied. In Section 3, we provide the Computational Details used in our study. In Section 4, we present the Results and Discussion of our first principles study of the kinetics and thermodynamics of QD growth from earliest stage precursors to > 1 nm magic sized clusters and provide projections about 3-5 nm quantum dot surface properties. Finally, we summarize our Conclusions in Section 5.

2. Model Curation

We now review the models we have selected to build up a first-principles understanding of growth from precursors and early-stage intermediates to nm-scale QDs. An early stage cluster (ESC) model was obtained from previous\textsuperscript{70} high-temperature ab initio molecular dynamics (AIMD) of In and P precursor mixtures. This cluster contains one P atom coordinated tetrahedrally by 4 In precursors along with two complexed In precursors that only coordinate to the neighboring In atoms (Figure 1a). The structure\textsuperscript{70} of this In\textsubscript{4}P tetrahedron is similar to the tetrahedral geometry of the zinc blende InP bulk crystal structure\textsuperscript{72}. We perform simulations on the X-ray crystal structure of a magic sized cluster (MSC) that was obtained by growing InP QDs with phenylacetate ligands\textsuperscript{43} (Figure 1d). This MSC structure has a surface comprising 16 excess In surrounding a near-1:1 InP core (21 In and 20 P) with geometric properties\textsuperscript{43} similar to the
ESC\textsuperscript{70}, albeit with reduced symmetry\textsuperscript{43, 55} in comparison to zinc blende InP\textsuperscript{72} (Figure 1b).

Carboxylate ligands are known\textsuperscript{28, 73} to form multiple binding modes to neighboring indium atoms on surfaces: bidentate carboxylate coordination to a single In center, as is common in isolated In(RCOO\textsuperscript{−})\textsubscript{3} precursors\textsuperscript{70}, or bridging ligands that coordinate multiple In centers in either a symmetric fashion with comparable distance to both In centers or asymmetrically in a manner that supports a partial second bond with one of the two In centers (Figure 1e). Monodentate coordination is not observed in equilibrium ESC or MSC structures but is expected to occur transiently during growth steps on the surface. It is useful to classify trends in reactivity and stability by binding mode.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Structures of InP clusters and elementary reaction steps studied in this work: a) AIMD-grown InP ESC with formate ligands; b) MSC In\textsubscript{37}P\textsubscript{20} without ligands; c) the MSC surface with formate ligands; d) the MSC surface with phenylacetate ligands; e) representative models of ligand binding modes; f) MSC rigid ligand dissociation (DE) for formate (R=H), acetate (R=CH\textsubscript{3}) and phenylacetate (R=CH\textsubscript{2}Ph); g) MSC In-O bond cleavage (\(\Delta E(\text{In-O})\)) for formate ligands; and h) PH\textsubscript{3} addition thermodynamics (\(\Delta E_{\text{rxn}}\), R to P) or kinetics (\(E_a\), R to TS). For all structures, atoms are colored as follows: In brown, P orange, O red, C gray, and H white.}
\end{figure}

The most common InP QD growth recipe\textsuperscript{18, 20-22, 41, 49, 74} employs myristic acid, a long
chain fatty acid, which has comparable electronic properties to shorter chain carboxylic acids, such as acetate or formate. To manage computational cost, we replace the phenylacetate ligands employed to stabilize the MSC in prior experimental work with both acetate and formate ligands and we compare to an ESC with acetate ligands also replaced by formate (Figure 1a,c and Supporting Information Table S1). We again employ PH₃ as our model precursor and discuss the effect of ligand precursor chemistry on our observations.

2b. Defining Elementary Steps of InP QD Growth.

The growth of InP QDs is a dynamic process comprising many individual steps. Prior reaction pathway analysis on high-temperature AIMD for ESC formation identified a consistent growth mechanism across reactions of individual precursors and larger ESCs. In both cases, it was observed that for an In-P bond to form, the In center must become undercoordinated through In-O bond cleavage in a coupled or sequential fashion. A nucleophilic oxygen atom from a carboxylate ligand then abstracts a functional group (here, a proton) from the phosphorus precursor. It is possible for this reaction to occur within a single complex of In and P precursors (i.e., an intracomplex reaction) or through assistance by a neighboring In precursor unit (i.e., intercomplex reaction). Regardless of the nature of the mechanism, In-O bond cleavage energies in small clusters were identified to be an essential predictor of In-P bond formation reaction energies across a wide range of ligand chemistries. In-O bond cleavage has also been hypothesized to occur experimentally when InP QDs are exposed to water. In this work, we investigate the range of surface chemistry and thus reactivity of both our computational ESC and the experimental MSC structures (Figure 1). Our goal in this work is to understand the heterogeneity in relative stability or, alternatively, reactivity toward continued growth of sites on model cluster and QD surfaces.
The simplest measure of site- and ligand- (i.e., phenylacetate, formate, and acetate) specific stability/reactivity trends on the surface of a QD model is the rigid ligand dissociation energy, $DE_i$. We compute the DE by removing the $i$th ligand from the QD surface and obtaining separate single point energies of the isolated ligand and modified QD for each ligand on the surface (Figure 1f).

Given the paramount importance$^{70-71}$ of In-O bond cleavage in overall reaction energetics for In-P bond formation, we also compute the energetic cost of cleaving the $i$th In-O bond, $\Delta E_i$(In-O), between an In surface site and the carboxylate ligand determined through partial relaxation of the cleaved ligand and comparison to the equilibrium QD energetics (Figure 1g and see Computational Details). For each ligand, we cleave the weaker In-O bond: the longer of two In-O bonds for chelating bidentate or symmetric bridging ligands and in asymmetric bridging ligands the longer In-O bond for the oxygen that forms two weaker bonds with both In centers (Figure 1 and Supporting Information Figure S1).

Following In-O bond cleavage, a likely elementary step for continued growth is the addition of PH$_3$ precursors to the In-rich surfaces (Figure 1h). The thermodynamics of this PH$_3$ addition provides a measure of the likelihood of continued QD growth at various reaction sites on the surface. We do not assume excess P precursor conditions$^{55}$ but use the PH$_3$ addition as a measure of site-specific reactivity. During AIMD, we observed$^{70}$ rapid formation of In-P(H$_2$)-In coordination following H abstraction from PH$_3$. Thus, we model PH$_3$ addition as the cleavage of an In-O bond at a bridging carboxylate site, proton abstraction by the free anionic carboxylate oxygen, and addition of a PH$_2$ moiety in the open In\textsuperscript{−}In site (Figure 1h). Addition at chelating bidentate sites is also considered with a similar mechanism, although it is energetically less favorable (see Sec. 4). We report the relative energy of PH$_3$ addition for each $i$th site,
$\Delta \Delta E_{\text{rxn},i}(\text{PH}_3)$, obtained from relaxation of the added PH$_3$ and protonated carboxylate, which typically dissociates from the surface, referenced against the value for an isolated precursor reaction (Figure 1 and Supporting Information Figure S2).

Although the kinetics of PH$_3$ addition are important, strong linear free energy relationships (LFERs) between reaction energies and barriers are frequently observed$^{75}$, including in reactions$^{71}$ between PH$_3$ and In precursors, permitting inference of kinetics from thermodynamic trends. To confirm LFERs on the MSC and ESC models, we compute select approximate transition states (TSes) for PH$_3$ addition (see Computational Details). We compute the $i$th site’s relative activation energy, $\Delta E_{a,i}$, on MSCs or ESCs with respect to an isolated precursor pair, where the TS is the highest minimum energy pathway structure obtained during PH$_3$ deprotonation by the free carboxylate (Figure 1h and Supporting Information Figure S2). In total, the steps pursued here are consistent with experimental observations of ligand exchange, and only some hypothesized pathways of MSC decomposition have been neglected.$^{34}$

3. Computational Details

Electronic structure calculations were carried out with TeraChem$^{76-77}$. Geometry optimizations$^{78}$ and path-based$^{79-80}$ TS searches were performed using density functional theory (DFT) with the hybrid B3LYP$^{81-83}$ exchange-correlation (xc) functional. The default B3LYP definition in TeraChem uses the VWN1-RPA$^{84}$ form for the local density approximation component of the correlation. All calculations were carried out with the composite LACVP* basis set, which corresponds to an LANL2DZ$^{85}$ effective core potential basis for In and the 6-31G* basis for the remaining atoms. Using a larger aug-cc-pVDZ basis set yields comparable reaction energies for PH$_3$ addition on representative cases (Supporting Information Figure S3). We validated our choice of xc functional and confirmed that alternative long-range corrected,
hybrid ωPBEh\textsuperscript{86} did not substantially change predicted reaction energies for PH\textsubscript{3} addition on representative cases (Supporting Information Figure S4).

Geometry optimizations were carried out using the DL-FIND\textsuperscript{78} module in TeraChem with the L-BFGS algorithm in Cartesian coordinates. Default thresholds of 4.5×10\textsuperscript{-4} hartree/bohr for the maximum gradient and 1.0×10\textsuperscript{-6} hartree for the change in energy were employed. For approximate TS searches and minimum energy pathways (MEPs) of PH\textsubscript{3} addition on the MSC and ESC models, initial guesses were provided for constrained optimizations followed by nudged elastic band (NEB)\textsuperscript{79-80} calculations. Activation energies (\(E_a\)) were determined with respect to a reactant in which a PH\textsubscript{3} precursor was 5 Å from the surface. Default NEB thresholds of 4.5×10\textsuperscript{-4} or 3.0×10\textsuperscript{-4} hartree/bohr for the maximum or root mean square (rms) of energy gradient, and 1.8×10\textsuperscript{-3} or 1.2×10\textsuperscript{-3} for the maximum or rms of the atomic displacement were employed. Twenty initial images were used in NEB, and 10 to 15 images were added after convergence then re-converged to ensure sufficient image density around the TS region. Inclusion of empirical dispersion correction (i.e., DFT-D\textsuperscript{387}) does not change trends for either DEs or ΔΔ\textsubscript{rxn} values (Supporting Information Figures S5-S6). Incorporation of thermodynamic corrections at 298.15 K does not change ΔΔ\textsubscript{rxn} values or trends (Supporting Information Table S2 and Figure S7). The 0 K electronic energies are instead reported throughout the main text due to high computational cost of thermodynamic corrections on the 261-924-atom models studied in this work (Supporting Information Table S1).

The X-ray crystal structure\textsuperscript{43} of the phenylacetate-ligated InP MSC ([In\textsubscript{37}P\textsubscript{20}(O\textsubscript{2}CCH\textsubscript{2}Ph)\textsubscript{51}]\textsuperscript{43}) was simulated along with acetate- ([In\textsubscript{37}P\textsubscript{20}(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{51}]\textsuperscript{43}) and formate- ([In\textsubscript{37}P\textsubscript{20}(O\textsubscript{2}CH)\textsubscript{51}]\textsuperscript{43}) ligated structures obtained by removing Ph and CH\textsubscript{2}Ph, respectively, H-atom capping, optimizing a constrained geometry in which only the H atoms were allowed to move.
An acetate-ligated ESC (In₆P(O₂CH)₁₅) from previous work was studied with formate ligands obtained by removing CH₃, H-atom capping, optimizing only the H atoms. Rigid ligand DEs on the MSC were computed for all three ligand types in bidentate and bridging ligands, whereas the remaining MSC and ESC quantities were computed only with formate ligands. Both a) ΔE(In-O) cleavage and b) ΔΔE_rxn addition energies were computed by i) cleaving one In-O bond, ii) H-capping the anionic O atom, and iii) carrying out a constrained geometry optimization in which only the hydrogenated ligand was free along with PH₂ for b). Model spherical InP nanoparticles were built using the supercell builder function in Avogadro on the experimental bulk InP structure and extracting spheres of target radii using an in-house script (Supporting Information Figure S8).

Atomic partial charges were obtained from the TeraChem interface with the Natural Bond Orbital (NBO) package. The Mayer bond order was calculated with Multiwfn.

4. Results and Discussion

4a. Rigid Ligand Dissociation Energies

As the MSC structure is most relevant to understanding QD growth processes, we first evaluate the rigid ligand DE from an MSC as a probe of surface reactivity and stability in InP QDs. DEs of the phenylacetate ligands on the MSC are both large in magnitude and span a 71 kcal/mol range, with lower DEs for the 12 chelating bidentate ligands (79-116 kcal/mol) than for the 39 bridging ligands (90-150 kcal/mol) regardless of symmetric (5) or asymmetric (34) binding mode (see Figure 1 and Supporting Information Table S3). Although coordination mode strongly influences the average DE, the large range of ligand DEs suggests differences in the local surface chemistry of the MSC play the dominant role. Indeed, mapping ligand DEs onto the MSC QD surface reveals heterogeneity in spatial distribution of high and low DE sites: both
extrema are surrounded by regions of ligands with intermediate binding energies (Figure 2 and Supporting Information Figure S9). Although site-specificity was previously suggested in ligand rearrangements on InP QDs43, these large variations in energetics are the first quantitative indication of heterogeneous growth rates at different sites on a QD surface.

**Figure 2.** Map of the range of 39 bridging ligand rigid DEs on the MSC for a) phenylacetate, b) acetate, and c) formate ligands all shown in the same view. The same inset color bar range is used for all three surfaces, as shown at top right. Representative low (top) and high (bottom) ligand dissociation structures are shown in inset with the In−−In separation labeled. A map with chelating bidentate ligands also shown is provided in Supporting Information Figure S9.

Qualitative observations for phenylacetate ligands are preserved in small (i.e., formate and acetate) ligands, consistent with observations that In-O bond energies are insensitive to chain length70 (see Figures 1-2 and Supporting Information Tables S1 and S3 and Figure S10).
Quantitatively, phenyl group bulkiness significantly weakens DEs relative to acetate two outlier cases that give phenylacetate a wider DE range than formate and acetate (Supporting Information Table S3 and Figures S10-S13). Formate and acetate DEs agree to within 5 kcal/mol, although maximum formate DEs are higher due to differences in interligand interactions for differing chain lengths (Supporting Information Tables S3-S5 and Figures S12-S13). Thus, we focus throughout this work on formate ligands to mitigate computational cost and expect that energetic and geometric trends inferred should be transferable to other carboxylate ligands, with minor underestimation of stability due to steric bulk in phenylacetate and overestimation of stability for formate (Figure 2).

Over the MSC structure, we observe a wide variation in geometric properties: In−In separations range from below 4 Å to nearly 5.5 Å and In-O surface-ligand bond distances vary from 2.08 Å to nearly 2.35 Å, motivating evaluation of possible correlations between energetics and geometry (Supporting Information Table S6). For the experimentally determined phenylacetate capped MSC, we observe moderate correlations of DEs to geometric properties (Supporting Information Figure S14). Bidentate and bridging ligand types exhibit a single (R²=0.48) correlation between increasing In-O bond length and decreasing DE and weakly positive correlations (R²=0.15-0.50) between increasing In−In separation and increasing DE for bridging ligands (Supporting Information Figure S14). For formate and acetate ligands, these geometric correlations are preserved (Supporting Information Figures S15-S16 and Tables S7-S9).

Although we have demonstrated correlations between energetic and geometric properties, we sought to explain the electronic structure origins of surface-ligand interactions by evaluating correlations between energetic and electronic properties. We therefore also evaluated: i) the
individual or summed Mayer bond valence (BV) of each In atom coordinated to the ligand, ii) the individual or summed Mayer bond orders of the In-O bonds, and iii) the partial charges of individual and ligand-summed carboxylate O atoms (Supporting Information Tables S6-S8). The In BVs represent the degree of bonding between surface In and any neighboring atoms (i.e., coordinating P in the QD or O from ligands). A wide range of summed In atom BVs (ca. 2.3-2.6) is observed, with average values about half (vs. 6) of what would be expected for purely covalent bonding, consistent with a picture of mixed ionic and covalent bonding \(^{43}\) (Supporting Information Tables S6-S8). Despite the expectation that the BV is a good indicator of average bonding strength of the In atom to its neighbors, no correlation is observed for individual or summed BVs and DEs (Supporting Information Figures S14-S16).

In contrast to BVs, we observe correlations between the phenylacetate In-O bond order and DEs and summed carboxylate O partial charges (Supporting Information Figure S14). A good correlation between DE and In-O bond order of the weaker of the two cleaving In-O bonds \((R^2=0.68)\) is observed, with very weak second bonds corresponding to the lowest DEs (Supporting Information Figures S1 and S14). This observation, which extends to acetate and formate ligands as well, suggests a picture in which the weakest interaction determines the overall DE because one weak bond is not compensated by strengthening of the other In-O bond (Supporting Information Figures S15-S16 and Tables S9-S10).

Regularized feature selection with LASSO \(^{94}\) confirms observations from univariate correlations: In-O bond distance, O atom partial charges, and the weaker bond In-O bond order are essential features (Supporting Information Table S11). The multiple linear regression model of the phenylacetate data has enhanced weighting of geometric properties and the formate model has a greater partial charge contribution, but all models have comparable rms errors (RMSEs) of
around 5-7 kcal/mol (4-7% of the mean DE, Supporting Information Table S11). Deviations between ligand types are not detectable from In-O-focused descriptors, which are well-correlated for differing ligands (Supporting Information Figure S17 and Table S12).

Overall, this analysis reveals that in InP QDs, local surface structure and interligand interactions can affect both ionic and covalent contributions to In-O bonds to lead to very large variations (ca. 50 kcal/mol or more) in ligand DEs across the MSC surface. We next consider the extent to which energetic variations and their electronic structure origins are consistent across lower energy (i.e., more probable) elementary steps in QD growth.

4b. In-O Bond Cleavage

Single In-O bond cleavage is a more realistic proxy\(^\text{70}\) for surface-site-specific reactivity, so we next consider whether trends observed for DEs hold for \(\Delta E(\text{In-O})\) on the MSC. Although we identified chelating bidentate DEs to be on average lower than the bridging DEs, we focus on \(\Delta E(\text{In-O})\) trends for bridging ligands (i.e., 39 of 51 MSC surface ligands). This choice is motivated by the fact that i) continued PH\(_3\) addition likely requires the two available In at bridging sites for PH\(_2\) coordination\(^\text{70}\) and ii) although DEs were lower for chelating bidentates than bridging ligands, \(\Delta E(\text{In-O})\) values are uniformly higher (Supporting Information Tables S13-S14).

As expected, \(\Delta E(\text{In-O})\) values are lower than DEs, but, somewhat surprisingly, the two quantities span a comparable range for bridging ligands (29-35 kcal/mol, Supporting Information Tables S8 and S13). A good correlation (\(R^2=0.59\)) is observed between \(\Delta E(\text{In-O})\) and DE, and most points fall within a ±3 kcal/mol range centered around the trendline (Figure 3). Mapping \(\Delta E(\text{In-O})\) on the InP surface reveals similar labile and stable spots distributed over the QD surface as was observed for DEs, owing to the good correlation of single and double bond
cleavage (See Figure 2 and Supporting Information Figure S18). The lower absolute $\Delta E$(In-O) values mean that some In-O bonds are twice as strong as others on the MSC surface, and only the weakest bonds are comparable to those (ca. 20 kcal/mol) in isolated precursors$^{70}$ (Figure 3). Thus, most of the MSC is expected to be less reactive than earlier stage clusters.

**Figure 3.** Correlation for 39 bridging (34 asymmetric in blue circles, 5 symmetric in red squares) formate ligands on an MSC between In-O bond cleavage ($\Delta E$(In-O), in kcal/mol) and rigid ligand dissociation energies (DE, in kcal/mol).

Although a good correlation is observed between $\Delta E$(In-O) and DEs, individual property-energy correlations differ: correlations with the electrostatic O atom partial charges or In-O bond distances are no longer present, whereas correlation to the In-O Mayer bond order is improved (Supporting Information Figure S19 and Table S9). At the same time, a previously observed weak correlation between formate DE and In$^{\cdots}$In internuclear separation is significantly strengthened (for 34 asymmetric ligands from $R^2=0.24$ to $R^2=0.75$), consistent with qualitative observations of short In$^{\cdots}$In separation producing lower $\Delta E$(In-O) values (see Supporting Information Figures S18-S19 and Table S9). Consistent with univariate analysis, feature selection confirms only the In-O bond order and In$^{\cdots}$In separation contribute significantly to determining $\Delta E$(In-O), with RMSEs for a two-variable linear model as low as 4.5 kcal/mol or around 12% of the mean (Supporting Information Table S15). Overall, these observations
suggest reorganization of the electronic structure on the other In-O bond following single In-O bond cleavage compensates for any electrostatic contribution to the bond cleavage that was observed in DE trends.

4c. PH$_3$ Addition Thermodynamics.

As with In-O bond cleavage, we observe that relative PH$_3$ addition reaction energies, $\Delta \Delta E_{\text{rxn}}$(PH$_3$), have a large variation over the MSC surface with labile and stable spots intermingled, although over a smaller range (15 kcal/mol for $\Delta \Delta E_{\text{rxn}}$(PH$_3$) vs. 29 kcal/mol for $\Delta E$(In-O)) of energies (see Figure 4 and Supporting Information Figure S20 and Table S13). We previously identified$^{70-71}$ that In-O bond cleavage was an essential predictor of In-P bond formation energetics in precursor and ESC reactions. Indeed, this observation holds for the MSC, where we observe a good correlation ($R^2=0.63$) between $\Delta \Delta E_{\text{rxn}}$(PH$_3$) and $\Delta E$(In-O) (Supporting Information Figure S20). For this reason, energetically unfavorable PH$_3$ addition at chelating bidentate sites was not pursued (Supporting Information Figure S21).

As would be expected from the close relationship between the two energetic quantities, correlation of $\Delta \Delta E_{\text{rxn}}$(PH$_3$) to underlying electronic and geometric properties is qualitatively equivalent to trends observed for $\Delta E$(In-O) (Figure 4 and Supporting Information Figure S22). That is, $\Delta \Delta E_{\text{rxn}}$(PH$_3$) correlates well to the In···In separation for symmetric ($R^2=0.99$) and asymmetric ($R^2=0.90$) bridging ligands, with all points falling within a $\pm$ 3 kcal/mol range around the trendline in an even stronger correlation than that was observed for $\Delta E$(In-O) (Figure 4). The observation that smaller In···In distances are associated with higher reactivity is at odds with expectations from bulk metal surfaces$^{95}$, where increasing metal-metal separation is known to make surfaces more reactive, not less so, highlighting unique qualities of covalent, directional bonding in III-V QDs. Given the substantial decline in thermodynamic favorability for
ΔΔE_{rxn}(PH_3) with increasing In••In separation, we also considered whether also allowing In sites to reorganize after PH_3 addition, initially neglected from our analysis, might alter our conclusions. For d(In••In) < 5.0 Å, we observe no change in optimized In••In distance and only modest (ca 0.1 Å) decreases in separation for some of the initial longer separation points. These modest rearrangements suggest the underlying core MSC or QD structure prevents significant changes in In••In separation that would reduce ΔΔE_{rxn}(PH_3) at high d(In••In) sites (Supporting Information Figure S23).

Figure 4. a) Relative reaction energies for PH_3 addition (ΔΔE_{rxn} in kcal/mol) with respect to an In precursor reference for 39 bridging ligands on a surface rendering of the MSC. The energetic range is shown by inset colorbar (green is low and orange is high), and structures with representative highest and lowest reaction energies are shown in the reactant state with relevant In-In distance labeled. b) Correlation of ΔΔE_{rxn} in kcal/mol versus In-In distance for 5 symmetric bridging bidentate ligand sites (red squares) and 34 asymmetric bridging bidentate ligand sites (blue circles) for the MSC (shown as gray solid lines with R^2 inset). Representative structures from a) are indicated in orange and green. The ESC ΔΔE_{rxn} for 2 symmetric ligands (light red squares) and 4 asymmetric ligands (light blue circles) are overlaid on top of the MSC correlations. A range of ±3 kcal/mol from the trendlines is shown in dashed gray.
The only other correlating property observed for $\Delta\Delta E_{\text{rxn}}(\text{PH}_3)$ is a single correlation ($R^2=0.73$) across both symmetric and asymmetric bridging ligands with the Mayer bond order of the weaker In-O interaction (Supporting Information Figure S22). This correlation is slightly strengthened over that observed for $\Delta E(\text{In-O})$, which is surprising because it may be expected that weakening In-O bonding reduces $\Delta E(\text{In-O})$, whereas PH$_3$ addition is a competition between In-O bond cleavage and In-P formation.

To confirm the generality of the correlation between In-In separation and $\Delta\Delta E_{\text{rxn}}(\text{PH}_3)$, we also computed PH$_3$ addition energies for sites on the ESC (Supporting Information Table S16). Of the 10 bridging ligand sites on the ESC, four (three symmetric, one asymmetric) have lower coordination numbers than observed for any MSC sites and are therefore much more reactive (Supporting Information Figure S24 and Tables S17-S18). For the remaining six bridging ligand sites (two symmetric and four asymmetric) on the ESC that have comparable coordination numbers to the MSC, overlaying the ESC energies and distances on the MSC data reveals a consistent relationship (light blue and red symbols in Figure 4 and see Supporting Information Table S16). As with the MSC, chelating bidentate ligands have large $\Delta E(\text{In-O})$ values and were therefore not considered for PH$_3$ addition (Supporting Information Table S19). These observations suggest that geometrically equivalent MSC and ESC sites are equally reactive, meaning that the subsurface core atoms are not perturbing the electronic structure of the In atoms beyond a nearest neighbor effect, although In-In separations sampled in the ESC are in some cases shorter than sampled in the MSC data or sites are more likely to be undercoordinated (see Supporting Information Figure S25).

Returning to the fact that across equivalent ESC and MSC sites $\Delta\Delta E_{\text{rxn}}(\text{PH}_3)$ correlates well to both In-In separation and Mayer bond order of the cleaving bond, we next considered if
there was a strong relationship between these two quantities that could rationalize surface reactivity and stability. Indeed, we observe two good correlations by ligand binding mode (symmetric: $R^2=0.89$, asymmetric: $R^2=0.75$) between increasing In–In separation and increasing In–O Mayer bond order (Supporting Information Figure S26). Thus, when In sites are further apart, these surface sites bind ligands more tightly. Since the bond strength in symmetric ligands is higher than in the asymmetric form, two distance-energy relationships are observed, but only one overall energy–bond-order correlation is needed, even across more tightly binding chelating bidentate ligands (see Figure 4 and Supporting Information Figures S26-S27).

4d. A Model for QD-size Dependent Reactivity.

To more directly probe why increasing the In–In separation strengthens the weaker In–O bond, we constructed a minimal model of two passivated In atoms and a bridging carboxylate in which we could control In–In separation in the asymmetric or symmetric bridging configurations (Figure 5 and Supporting Information Figures S28-S29). Good correspondence is observed between minimal model bond orders and those in the MSC and ESC, despite differences in chemistry due to the In atoms being isolated instead of on an InP cluster (Figure 5 and Supporting Information Figure S26). In asymmetric ligands, increasing In–In separation above 4.25 Å (i.e., most distances sampled on the MSC) strengthens the weaker of the two In–O bonds because the O atom that was partially bonded to two In centers is now only close enough to the single In center, whereas compression below 4.25 Å increases the Mayer bond order again as the bonding redistributes between the two In centers (Figure 5 and Supporting Information Figure S28). Conversely, for symmetric bridging ligands, increasing In–In separation increases bond order monotonically (Supporting Information Figure S29). These observations explain the higher bond orders observed in short In–In separation ESC sites not sampled on the MSC (Supporting
Information Figures S26 and S28).

**Figure 5.** In-In separation (Å) versus In-O Mayer bond order for 34 asymmetric (blue filled circles) and 5 symmetric (red filled squares) MSC formate ligands. Bond orders from a simplified model (symmetric and asymmetric shown at top) obtained from constrained variation of In-In separation are shown as white symbols with a ± 0.03 bond order range (shaded region).

Given the strong variations in surface reactivity of MSC sites but consistency with equivalent sites on the even smaller ESC, we next developed a model of how surface morphology is likely to evolve during QD growth (Supporting Information Text S1). We expect the depletion of reactive surface sites to coincide with the slowing or cessation of QD growth. In addition to the MSC crystal structure, experimental mass spectrometry has quantified\textsuperscript{48} the number of core and surface In atoms in five QD sizes ranging from 2.42 to 3.28 nm in diameter, which is roughly twice the diameter of the MSC\textsuperscript{43} and a typical size for InP QDs\textsuperscript{19, 36, 48} (Supporting Information Table S20). These QDs have an In-rich surface with comparable core densities to spherical NPs extracted from bulk crystalline InP (Supporting Information Text S1 and Table S21 and Figures S8 and S30).

During growth from an ESC to MSC to QD, the relative excess surface In decreases, increasing average In-In surface separations, $d_{av}(\text{In-In})$ (Supporting Information Text S1 and
Figure 6). The ESC $d_{av}(\text{In}^{-}\text{In}) = 4.13$ Å is the same as that in an In-terminated bulk spherical model ($d_{av}(\text{In}^{-}\text{In}) = 4.14$ Å), indicating that at the earliest stages of growth the surface is maximally In-rich (Figure 6 and Supporting Information Table S21). In comparison, the MSC $d_{av}(\text{In}^{-}\text{In}) = 4.75$ Å is already indicative of a less In-rich surface (Figure 6). Additionally, a higher ratio of symmetric:asymmetric bridging sites is observed in the ESC (5 of each, i.e., 1:1) than in the MSC (5:34) (Figure 6). We then developed a geometric model of QD surface area to predict $d_{av}(\text{In}^{-}\text{In})$ in the MALDI-TOF-characterized QDs (Supporting Information Text S1 and Figure S31 and Table S22). The less In-rich surface of QDs leads to an even larger $d_{av}(\text{In}^{-}\text{In}) = 5.56$-5.77 Å, with increasing values for increasing QD size (Supporting Information Table S22).

Figure 6. Distributions of In-In distances on the ESC, MSC, and a 3.28 nm QD. Normalized and smoothed surface In-In distance distributions are shown for the InP MSC (solid, gray line) and an InP quantum dot (QD) (solid, green line). Each individual surface In-In distance is shown for the ESC (solid, orange, sticks). Average In-In distances in the ESC (dashed, orange), MSC (dashed, gray), and QD (dashed, green) are also indicated. The estimated reaction energies based on the linear best-fit line of reaction energies relative to the In(HCOO)$_3$ reference are shown with light blue (lowest energy) to light red (highest energy) shaded regions for the MSC and QD distributions, as indicated by the inset color bar. Structural models of average MSC and QD In$^{-}$In separation are shown at top.
Noting that we have information not just about $d_{av}(\text{In}^{-}\text{In})$ for the MSC but all In$^{-}$In separation values on the surface, we smoothed the distribution to show the essential features (Supporting Information Text S1 and Table S23). Overall, two distinct populations are observed of short In$^{-}$In separations (3.5-4 Å) with symmetric carboxylate ligands and a broader distribution peaked slightly above $d_{av}(\text{In}^{-}\text{In})$ for the asymmetric ligands (Figure 6). As we have seen, increasing In$^{-}$In separation leads to a rapid decline in favorability for continued PH$_3$ addition (Figures 4 and 5). Assuming that the observations of i) decreased reactivity with increasing In$^{-}$In separation and ii) qualitative features of the MSC distance distribution hold in larger QDs, it should be possible to predict relative surface reactivity of larger (i.e., 3.28 nm$^{48}$) QDs (Figure 6 and Supporting Information Text S1 and Figure S32 and Table S24). By taking experimentally-known surface $d_{av}(\text{In}^{-}\text{In})$ and modeling possible distributions of the sites, we observe that the population of thermodynamically favorable addition sites are dramatically reduced in both absolute and relative quantities (only 1.8% or 3 sites should have $\Delta\Delta E_{\text{rxn}}(\text{PH}_3) < 30$ kcal/mol) in comparison to the MSC and ESC (Figure 6). This analysis is robust to the approximations we have made such as assuming a continuing increase in ratio of asymmetric bridging to symmetric bridging ligands (from 1:1 in the ESC to 7:1 in the MSC to 10:1 in Figure 6, see other models in Supporting Information Text S1, Figures S33-S35, and Tables S25-S26). The persistence of the MSCs during growth$^{34, 43, 48}$ is consistent with our analysis and can be understood in terms of a low fraction of most reactive sites. The very persistent (i.e., stable) MSC sizes (i.e., 1.1-1.3 nm$^{42-43}$) and stoichiometries observed in InP QD growth$^{48}$ appear to correspond to configurations that have low concentrations of sterically-accessible and reactive symmetric bridging ligands.

The decreased number of short In$^{-}$In separation points on the surface of a mature QD
can be rationalized by geometric arguments. In the MSC, bridging carboxylate ligands, be they symmetric or asymmetric in their binding, can coordinate two neighboring In sites flexibly for In–In separations ranging from as little as around 3 Å (MSC min. is 3.8 Å) to as high as around 6.5 Å (MSC max. is 5.3 Å) due to the 2.9 Å separation between the carboxylate O atoms (Supporting Information Figure S32). Conversely, a single P precursor must insert between two In atoms for continued growth in a much narrower range (3.6-5.2 Å) of theoretically possible In–In separations. These geometric constraints could rationalize why addition of excess phosphorus precursor to an MSC produces a distinct non-zincblende structure. Therefore, growth should terminate in In-rich surfaces with large In–In separations passivated by bridging carboxylates because any site where a P precursor can attack will be a favorable site for continued In addition. Careful selection of alternate In and P ligand precursor chemistries beyond carboxylates for In precursors should then be expected to change both the nature of growth and of the surface termination.

4e. Relationships between Growth Thermodynamics and Kinetics.

Thus far, our focus has been on thermodynamic quantities, which are most relevant for slow growth conditions. If strong scaling relationships hold between kinetic (i.e., $E_a$) and thermodynamic (i.e., $\Delta E_{\text{rxn}}$) quantities, then all of the thermodynamic analysis will apply to kinetically limited regimes. We had previously observed good scaling relationships for precursor reactions, but we now test if this relationship holds on larger clusters. We explicitly compute reaction pathways for $\text{PH}_3$ addition on five (i.e., half of all possible) representative bridging ligand sites on the ESC (Supporting Information Text S2). In comparison to an intracomplex precursor reaction, $\text{PH}_3$ addition on these ESC sites was thermodynamically less favorable for most cases. The minimum energy pathway (MEP) characterization includes i)
cleavage of an In-O bond, ii) insertion of PH$_3$ between two In sites, iii) simultaneous proton abstraction from the substrate, and iv) formation of two In-P bonds (see Computational Details).

When carried out sequentially, the In-O bond cleavage step comprises most of the full abstraction and In-P bond formation barrier$^{70-71}$ (Figure 7 and Supporting Information Figure S36). Good kinetic correspondence between ESC and precursor pathways is observed for cases where the thermodynamics are comparable (blue versus red lines in Figure 7b).

**Figure 7.** a) $\Delta E_a$ versus $\Delta\Delta E_{rxn}$ (both in kcal/mol) with respect to an In(HCOO)$_3$ precursor reference (empty red square) for PH$_3$ addition on five representative sites on the ESC (blue circles) with a best-fit line (black, dashed) shown. b) Absolute ESC PH$_3$ addition reaction coordinate shown for case with asterisk indicated in a) in blue compared to absolute intracomplex precursor reaction energetics in red. Relevant structures on the ESC reaction pathway, i.e., In-O bond cleavage and H abstraction, are shown with relevant distances in each step annotated. The exchanged ligand, PH$_3$ molecule, and associated In atoms are opaque, whereas the neighboring environment is translucent. The energetics of an intracomplex In(HCOO)$_3$ precursor reaction reference are indicated in red.

For all MEPs, P-H bond shortening and O-H bond elongation is observed simultaneously as a proton is transferred to the anionic carboxylate oxygen (Supporting Information Figures S36-S37). Higher barriers correspond to cases where the In-P bonds do not shorten significantly or do so only after the abstraction step, whereas low barrier cases exhibit In-P bond formation during proton abstraction (Figure 7 and Supporting Information Figure S37). The most favorable surface sites for addition enable i) In-O bond cleavage and rotation of the carboxylate away from the surface, ii) alignment of the carboxylate O$^-$···H$^-$P transferring atoms to a near 180$^\circ$ angle, iii)
a shortened O’ to P separation to enable proton sharing in the TS, and iv) concomitant formation of a shorter (i.e., ~ 2.6-2.8 Å) partial In-P bond for the In site that is no longer bonded to the carboxylate (Figure 7 and Supporting Information Figure S37). If In−−In separation is too large, In-P bonds cannot form during the abstraction process, helping to explain the good scaling relationship between the thermodynamics and kinetics in these systems (Figure 7a). Importantly, calculation of the MEPs on three representative MSC sites yields relative $E_a$s consistent with the scaling relation observed for ESC sites (Supporting Information Figures S38-S39 and Text S2).

Thus, an overall picture emerges in which carboxylate coordination to In sites is more flexible than PH$_3$ addition, suggesting that both kinetics and thermodynamics are unfavorable for continued addition to the In-rich surface once In sites are fully coordinated and well-separated on the surface. This concept could be used to extend qualitative kinetic growth models$^{36}$ to directly account for increase in average In−−In surface separations with continued growth, although we note that instantaneous separations can vary widely as QDs grow.

5. Conclusions

We developed first-principles-derived models that unify InP QD formation from the isolated precursor and early stage cluster reactions to 1.3-nm magic size clusters and used these observations to rationalize experimentally observed properties of full sized > 3 nm quantum dots. First-principles modeling on the experimentally characterized, 1.3-nm MSC surface revealed large surface-dependent reactivity for all elementary growth process steps including full ligand dissociation, single In-O bond cleavage, and PH$_3$ addition. Overall observations revealed that fundamental steps could be as much as twice as energetically costly even between neighboring surface sites. These thermodynamic trends were observed to correlate well to kinetic properties, supporting our assignment of labile and stable spots from either a thermodynamic or kinetically
Correlation of electronic or geometric structural properties to energetics identified surprising sources for these variations in reactivity. Namely, short In–In separation on the surface correlated to the most reactive sites, which was explained by decreasing ligand-surface bond strength in these cases, as judged through bond order metrics derived directly from the In-O bond density. Increasing In–In separation led to more favorable covalent bonding orientation between carboxylate ligands and surface In atoms. This III-V reactivity deviates from typical models for more ionic II-VI QD growth mechanisms. We confirmed that large In–In separation remained favorable for carboxylate binding whereas P precursors were unlikely to favorably add to such sites. This observation was especially surprising because it is at odds with conventional understanding that strain in bulk metallic surfaces increases reactivity. The connection described between structure and reactivity provides a geometry-based method to assess the growth and reactivity of experimentally characterized InP clusters and QDs without further simulation.

The unique constraints of carboxylate or P precursor binding to In atoms rationalized why all sizes of InP clusters and QDs are In-rich but become less so as QDs mature. These observations also point to the importance of the geometric structure of both In and P precursors in considering alternate growth recipes to control both kinetics as well as surface morphology in III-V QDs. In the future, these constraints and energetics could be incorporated into kinetic models to develop a predictive understanding of how to control III-V QD growth through altered ligand chemistries or concentrations.

ASSOCIATED CONTENT

Supporting Information Available:
Basis set, empirical dispersion, and exchange-correlation functional testing; thermodynamic correction effects on reaction energies; properties and estimations of surface coverage on bulk-cut and experimental models of InP QDs; peak fitting for estimating distribution of In-In distance on various larger QD models; maximum possible In-In distance on QD surfaces; full dissociation energies of ligands for formate, acetate, and phenylacetate ligands on the MSC; correlations of rigid ligand dissociation and single bond dissociation; schematics of structures used to classify ligand types; effect of optimization on In-In distances; correlations of PH3 addition energies, single bond cleavage energies, or rigid ligand dissociation energies with various electronic and geometric properties; relationship between In-In distance and Mayer bond order; feature selection for property to energy correlations; summary of all correlations observed between energies and properties; ESC relative PH3 addition energies; outlier ESC reaction energies and coordination number analysis; minimum energy pathways and structures on relevant ESC sites; minimum energy pathways and structures on relevant MSC sites (PDF)

Structures of simplified ESC, MSC with three ligand types, and bulk cut QD models (ZIP)

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Notes

The authors declare no competing financial interest.

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