

Article

Structural Evolution and Optoelectronic Properties of Ga_xN_x Nanostructures: From Cubic to Hexagonal Configurations

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Abstract

In this work, the structural, electronic, optical, and vibrational properties of gallium nitride (Ga_xN_x) nanostructures were systematically investigated using density functional theory (DFT) and time-dependent DFT (TD-DFT). A series of nanoparticles was constructed starting from a cubic-like Ga_4N_4 building unit, leading to one-dimensional (1D), two-dimensional (2D), three-dimensional (3D), and hexagonal configurations. Geometry optimizations and vibrational frequency calculations were performed at the B3LYP/def2-TZVP level, while optical properties were investigated using TD-DFT with the CAM-B3LYP functional. Only dynamically stable structures without imaginary vibrational frequencies were considered for spectroscopic analysis. The results reveal a strong dependence of the optical and vibrational behavior on nanoparticle size and geometry. Larger and lower-symmetry systems exhibit broader and red-shifted UV–Vis absorption spectra together with richer IR vibrational features. In contrast, elongated low-dimensional configurations such as $\text{Ga}_{12}\text{N}_{12}$ –1D and $\text{Ga}_{16}\text{N}_{16}$ –1D/2D were found to be dynamically unstable. The investigated nanostructures also show a clear tendency toward structural reorganization from cubic-like motifs to compact hexagonal arrangements related to the wurtzite phase of bulk GaN. Benchmark analysis demonstrates that CAM-B3LYP provides reliable excitation energies at moderate computational cost. Overall, the obtained results highlight the strong coupling between structure and optoelectronic properties in Ga_xN_x nanostructures and indicate their potential for nanoscale optoelectronic and photonic applications.

Keywords: gallium nitride nanoparticles; density functional theory; time-dependent DFT; optical absorption; infrared vibrational spectra; hexagonal nanostructures; nanoclusters

1. Introduction

The continuous increase in global energy demand, together with the environmental impact associated with fossil fuel consumption, has intensified the search for advanced materials with improved efficiency and reduced environmental footprint [1,2]. In this context, semiconductor nanostructures have attracted significant attention due to their size-dependent physical and chemical properties, which differ substantially from those of bulk materials. These nanoscale systems exhibit tunable electronic structure, enhanced optical response, and increased surface reactivity, making them promising candidates for applications in optoelectronics, sensing, and energy-related technologies [3,4].

Among III–V semiconductor materials, gallium nitride (GaN) is particularly important because of its wide band gap, excellent thermal and chemical stability, and favorable electronic properties [4,5]. GaN-based materials are widely used in light-emitting diodes (LEDs), laser diodes, high-frequency electronic devices, and ultraviolet photodetectors [6,7].



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At the nanoscale, GaN nanostructures exhibit pronounced quantum confinement effects, leading to significant modifications of their electronic and optical behavior [8]. These characteristics make GaN nanoparticles attractive for next-generation nanoscale photonic and sensing applications [9–11].

Recent theoretical and experimental studies have focused on understanding the relationship between structure, size, and physical properties in semiconductor nanostructures [12]. Density Functional Theory (DFT) has been extensively used for investigating structural, electronic, and vibrational properties, while Time-Dependent DFT (TD-DFT) has proven effective for predicting optical absorption spectra and excited-state behavior [13,14]. In particular, hybrid and range-separated exchange–correlation functionals, such as B3LYP [15] and CAM-B3LYP, provide reliable descriptions of vibrational frequencies and electronic excitations, respectively [16,17].

Previous studies on related semiconductor nanostructures, including AlN [18], Mg-based compounds (MgS, MgSe, MgTe) [19], and Sc-based systems [20], have shown that the extension of cubic-like building units can generate a variety of stable one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) configurations. These investigations demonstrated that dimensionality and symmetry strongly influence the electronic structure, optical absorption, and vibrational response of semiconductor nanoparticles [21]. In particular, low-symmetry and elongated structures often exhibit broadened and red-shifted optical spectra together with richer vibrational features [22,23]. Experimental investigations on GaN nanoparticles have also reported optical features in the ultraviolet and near-visible spectral regions that depend strongly on particle size and structural characteristics. For example, photoluminescence measurements of GaN nanoparticles with sizes between 10 and 22 nm revealed emission peaks at approximately 2.85 and 3.0 eV [22]. These observations highlight the strong relationship between nanoparticle structure and optical response and provide useful experimental reference points for theoretical investigations of GaN nanostructures.

Despite extensive research on bulk and low-dimensional GaN systems, a systematic investigation of GaN nanoclusters focusing on the combined effects of size, geometry, and dynamical stability on their optical and vibrational properties remains limited [23]. In particular, the structural evolution of GaN nanoparticles from cubic-like motifs toward alternative geometries has not been fully explored.

In the present work, a comprehensive theoretical study of Ga_xN_x nanostructures is performed using DFT and TD-DFT methods. A series of nanoparticles was constructed starting from a cubic-like Ga_4N_4 building unit and subsequently extended along different spatial directions, leading to 1D, 2D, and 3D configurations, as well as explicitly constructed hexagonal geometries. Structural stability was evaluated through vibrational frequency analysis, while optical properties were investigated using simulated UV–Vis absorption spectra.

Particular emphasis is placed on the interplay between geometry and stability. Several elongated cubic-derived configurations were found to exhibit imaginary vibrational frequencies, indicating dynamical instability, whereas larger systems tend to reorganize into more compact hexagonal-like arrangements. This behavior is consistent with the known preference of GaN for the wurtzite phase and highlights the important role of structural organization in determining the optoelectronic properties of GaN nanostructures [6].

The B3LYP functional was selected for geometry optimization and vibrational analysis because it provides reliable structural parameters, stable convergence behavior, and accurate vibrational frequencies for semiconductor nanoclusters at moderate computational cost. Previous studies on related III–V semiconductor nanostructures have also demonstrated the suitability of B3LYP for describing equilibrium geometries and bonding characteristics.

More computationally demanding hybrid functionals, such as HSE06, were not considered due to the large size and number of investigated nanostructures.

The novelty of the present work lies in the systematic investigation of a broad family of Ga_xN_x nanostructures covering different sizes, dimensionalities, and geometrical motifs within a unified computational framework. Unlike previous studies that typically focused on isolated GaN clusters or a single structural family, the present work combines cubic-derived, low-dimensional, cage-like, and explicitly constructed hexagonal nanostructures. Particular emphasis is placed on the relationship between geometry, dynamical stability, optical absorption, and vibrational properties, as well as on the structural evolution from cubic-like arrangements toward hexagonal configurations related to the wurtzite phase of bulk GaN.

Overall, the present study provides a systematic analysis of the structure–property relationships in Ga_xN_x nanoparticles and offers insight into the effects of size, geometry, and dimensionality on their stability and spectroscopic behavior. The obtained results contribute to the understanding and rational design of GaN-based nanomaterials for optoelectronic and energy-related applications.

2. Computational Details

The structural, electronic, and optical properties of a series of GaN-based nanostructures were investigated using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods [24–26]. A variety of nanoparticle geometries was constructed starting from an initial cubic-like building unit, which was subsequently extended along one, two, and three perpendicular directions to generate one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) configurations. The selected structural motifs were inspired by previous studies on AlN-, ScN-, and MgS-based nanostructures, where similar construction approaches led to stable geometries with distinct optoelectronic behavior [18–20].

All geometry optimizations were performed using the B3LYP exchange–correlation functional [15] in combination with the def2-TZVP triple- ζ valence plus polarization basis set [24]. Harmonic vibrational frequency calculations were carried out at the same level of theory in order to evaluate the dynamical stability of the optimized geometries and analyze their vibrational properties. Structures without imaginary frequencies were identified as stable local minima on the potential energy surface.

The def2-TZVP basis set [24] was selected because it represents a well-established triple- ζ basis with polarization functions and has been extensively employed in DFT and TD-DFT studies of semiconductor nanostructures. The chosen basis set provides a reasonable compromise between computational accuracy and cost, particularly for the larger systems investigated in the present work. Performing similar convergence optimization tests as in the previous comment for the Ga_4N_4 NP, we found that the energies of the final geometries obtained with def2-svp and def2-tzvp differ by less than 0.5 mHa. That shows the def2-tzvp basis set works very well.

TD-DFT was employed because it provides an efficient and computationally tractable approach for the calculation of excited-state properties and optical spectra of nanoscale systems. The present study is primarily concerned with relative trends in excitation energies and optical absorption features across different Ga_xN_x nanostructures, for which TD-DFT has been shown to provide reliable qualitative and semi-quantitative predictions. Nevertheless, TD-DFT may exhibit limitations in the description of strongly correlated excited states, multi-reference systems, and long-range charge-transfer excitations. The use of the CAM-B3LYP functional partially alleviates these limitations through the inclusion of long-range exchange corrections. It should be noted that M062X functional gave also very

good comparison with the EOM-CCSD, however the CAMB3LYP functional was chosen because it was used for ALN nanostructures [18].

It should be noted that the Ga₄N₄ cluster was employed as a representative benchmark system for evaluating the relative performance of the examined exchange–correlation functionals. Due to the rapidly increasing computational cost of EOM-CCSD calculations [27] for larger Ga_xN_x nanostructures, direct benchmarking was not feasible for all investigated systems. Therefore, the benchmark should be regarded as a practical validation approach rather than a universal assessment of all cluster sizes and geometries.

The calculated optical trends are also consistent with previously reported theoretical and experimental studies on GaN nanostructures, which generally exhibit strong ultraviolet absorption and geometry-dependent spectral shifts associated with quantum confinement and structural effects.

The simulated absorption spectra were generated by representing each electronic transition with a Gaussian function centered at the corresponding excitation energy using a broadening parameter of 0.1 eV. Similarly, the vibrational spectra were obtained by applying Gaussian broadening with a standard deviation of 10 cm^{−1} to each calculated vibrational mode [28].

All DFT and TD-DFT calculations, including geometry optimizations, vibrational analyses, and optical spectra simulations, were performed using the TURBOMOLE software package [29,30]. In addition, selected benchmark calculations were carried out using Gaussian [28], due to its efficient implementation of correlated wavefunction methods.

The investigated geometries included linear, planar, and asymmetric configurations, such as L-, T-, and S-shaped structures, enabling a systematic analysis of the effects of size, dimensionality, and symmetry reduction on the structural and spectroscopic properties of GaN nanostructures.

3. Results and Discussion

Benchmark calculations were first performed on the prototype Ga₄N₄ cluster in order to validate the selection of the exchange–correlation functional for the investigation of Ga_xN_x nanostructures [16]. The calculated lowest singlet excitation energies and oscillator strengths obtained using different functionals are summarized in Table 1. Although excitation energies from the EOM-CCSD method were available and used as reference values, the corresponding oscillator strengths were not evaluated at this level of theory [27].

Table 1. The Ga₄N₄ NP comparison of the first excitation energy for the different functionals.

Functional	1st Excitation (eV)	Oscillator Strength
B3LYP	0.349	0.0045
CAM-B3LYP	0.714	0.0102
PBE0	0.550	0.009
M06-2X	0.967	0.012
EOM-CCSD	0.843	-

Although M06-2X exhibited a marginally smaller deviation for the first excitation energy of Ga₄N₄, CAM-B3LYP was selected due to its balanced overall performance, long-range correction, and reliable description of optical excitations in semiconductor nanostructures.

Among the examined functionals, CAM-B3LYP provided excitation energies in very good agreement with the high-level EOM-CCSD results, supporting its suitability for describing excited states in Ga_xN_x nanostructures. It should be noted that exploratory calculations performed with the pure GGA-PBE functional failed to converge reliably for

the Ga_4N_4 system at both the geometry optimization and excited-state levels. Consequently, PBE results were not included in the benchmark comparison, whereas the hybrid PBE0 functional converged successfully and its results are reported in Table 1. This behavior reflects the known limitations of pure GGA functionals in describing electronically delocalized excited states and small semiconductor clusters [31].

Based on these observations, B3LYP was employed for geometry optimizations and vibrational analyses due to its stable convergence behavior and reliable structural description [15], while CAM-B3LYP was selected for the TD-DFT calculations of optical properties. This combination provides an effective balance between computational efficiency and accuracy for the investigated systems.

The obtained benchmarking results are consistent with previous studies on III–V semiconductor nanostructures, including AlN and ScN nanoparticles, where CAM-B3LYP successfully reproduced excitation energies at substantially lower computational cost compared to high-level ab initio methods [18,20]. Similar behavior has also been reported for MgS nanostructures [19].

Overall, the benchmark analysis validates the adopted computational framework for the systematic investigation of the structural, vibrational, and optical properties of Ga_xN_x nanostructures.

For geometry optimization, the functional is not very important. Indeed, that was confirmed for the Ga_4N_4 NP. By using as initial guess the geometry obtained from B3LYP, we performed geometry optimization with different functionals. The energies of the final structures were less than 6 mHa different from the initial guess (B3LYP) indicating that the geometry obtained from the B3LYP is almost the same as the one obtained with all the other functionals.

3.1. Ga_xN_x Nanostructures

Following the benchmarking analysis, the optimized geometries of the Ga_xN_x nanostructures were systematically examined in order to investigate the effects of size, dimensionality, and structural organization on their stability and spectroscopic behavior. Starting from an initial cubic-like Ga_4N_4 building unit, a series of nanostructures was generated through elongation along different spatial directions, leading to one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) configurations [32].

During geometry optimization, several structures underwent significant structural rearrangements and partially deviated from their initial cubic-like motifs. In particular, larger systems such as $\text{Ga}_{24}\text{N}_{24}$ exhibited the formation of extended hexagonal-like arrangements, consistent with the known preference of GaN for wurtzite-related coordination [33,34]. For even larger nanostructures, including $\text{Ga}_{32}\text{N}_{32}$ and $\text{Ga}_{36}\text{N}_{36}$, the optimized geometries evolved toward compact cage-like morphologies [35,36].

Based on their size and structural characteristics, the investigated Ga_xN_x nanostructures are discussed in the following sections according to their geometry and dimensionality.

3.1.1. Size- and Geometry-Dependent Properties of Ga_8N_8 and $\text{Ga}_{16}\text{N}_{16}$ Nps

The first group of Ga_xN_x nanostructures examined in this study consists of the Ga_8N_8 cluster and the larger $\text{Ga}_{16}\text{N}_{16}$ systems with different geometrical configurations (T-, S-, L-, and L3-type), as illustrated in Figure 1. Starting from the initial cubic-like building unit, elongation along different spatial directions generated a variety of morphologies with distinct symmetry characteristics.

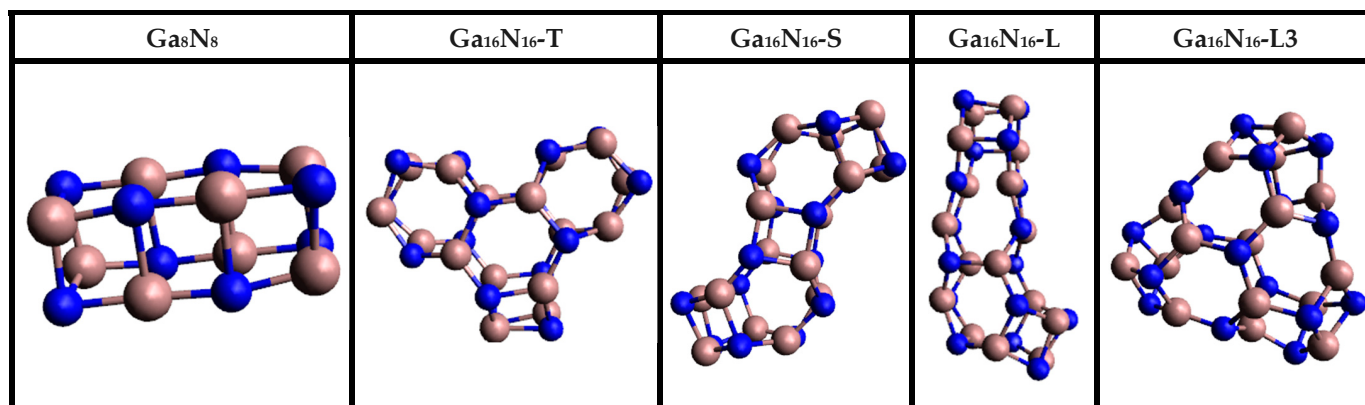


Figure 1. Optimized geometries of Ga_8N_8 and $\text{Ga}_{16}\text{N}_{16}$ nanostructures illustrating the effect of size increase and structural variation (T-, S-, L-, and L3-type). Gray spheres correspond to Ga atoms, while blue spheres represent N atoms.

The Ga_8N_8 cluster serves as a reference system, retaining a compact and nearly cubic three-dimensional geometry with relatively high symmetry. In contrast, the $\text{Ga}_{16}\text{N}_{16}$ nanostructures exhibit increased structural flexibility and reduced symmetry, resulting in more complex atomic arrangements [32,33]. The optimized geometries reveal a progressive transition from symmetric to distorted configurations, with the T-type structure remaining relatively compact, while the S-, L-, and L3-type geometries display more pronounced structural distortions. In several cases, partial hexagonal-like motifs begin to emerge, indicating the initial tendency of GaN systems toward structural reorganization [32].

To investigate the relationship between structure and physical properties, both the optimized geometries and the corresponding spectroscopic responses were analyzed. Structural visualization was performed using Avogadro, while the calculated UV–Vis absorption and IR spectra were processed and represented using MATLAB R2025a.

The differences in geometry are directly reflected in the optical response of the examined nanostructures, as shown in Figure 2. The Ga_8N_8 cluster exhibits a relatively simple absorption spectrum dominated by a strong transition in the high-energy region around 3.8–4.0 eV, accompanied by weaker features near ~2.0 and ~3.2 eV. In contrast, the $\text{Ga}_{16}\text{N}_{16}$ structures display significantly broader and denser spectra, with multiple electronic transitions distributed approximately between 2.2 and 5.0 eV. This behavior is associated with the larger size and lower symmetry of the clusters, which increase the density of accessible electronic states.

Among the investigated geometries, the T-type structure shows intense absorption mainly in the 4.3–5.0 eV region, with a dominant peak near 4.4–4.5 eV, whereas the S-type configuration exhibits broader spectral features extending over a wider energy range. The L- and L3-type geometries present similarly rich spectral profiles, with enhanced absorption in the 4.3–4.7 eV region, demonstrating the strong influence of morphology on the electronic excitation behavior.

A similar evolution is observed in the vibrational spectra. The Ga_8N_8 cluster is characterized by a limited number of IR-active modes, primarily associated with Ga–N stretching vibrations in the 450–600 cm^{-1} region. For the $\text{Ga}_{16}\text{N}_{16}$ nanostructures, the spectra become considerably richer, with a dense distribution of vibrational modes extending mainly between 500 and 900 cm^{-1} . The S-type geometry exhibits the most intense high-frequency peak near ~890 cm^{-1} , while the L- and L3-type structures display dominant modes in the 800–850 cm^{-1} region. The T-type configuration presents a broader vibrational distribution, indicating stronger coupling between local and collective vibrational motions.

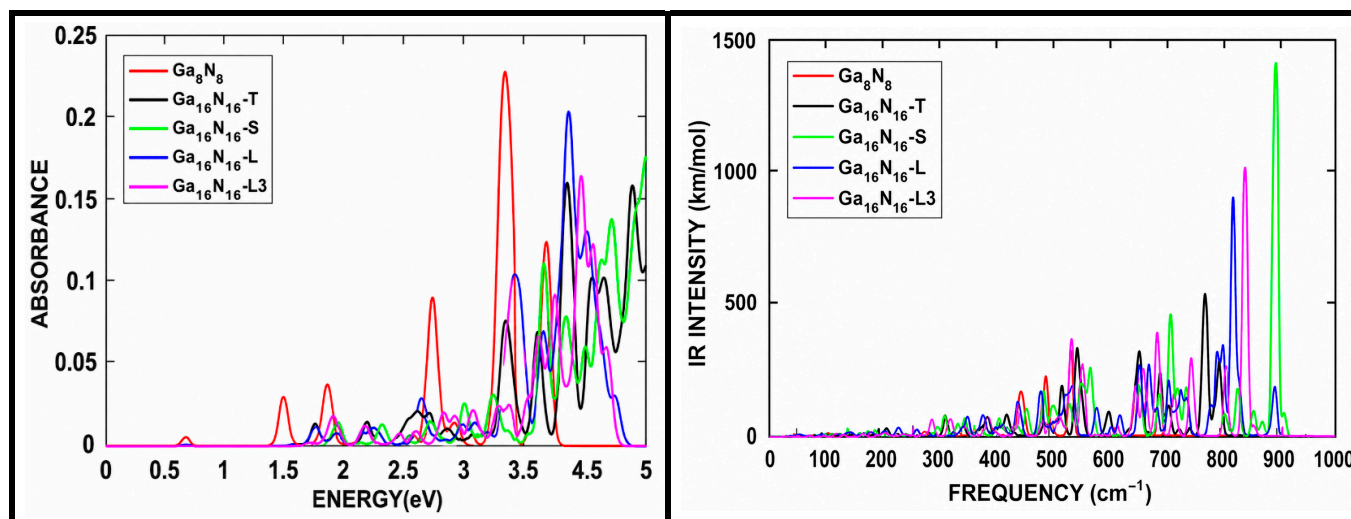


Figure 2. Calculated UV–Vis absorption and IR vibrational spectra of Ga_8N_8 and $\text{Ga}_{16}\text{N}_{16}$ nanostructures with different geometrical configurations (T-, S-, L-, and L3-type), illustrating the influence of size increase, structural distortion, and symmetry reduction on the electronic transitions and vibrational response of the examined Ga_xN_x systems.

Overall, the transition from the symmetric Ga_8N_8 cluster to the more distorted $\text{Ga}_{16}\text{N}_{16}$ configurations leads to broader absorption spectra, increased vibrational activity, and enhanced spectral complexity. These effects originate primarily from symmetry reduction and structural expansion, which favor a larger number of allowed electronic and vibrational transitions. Structures exhibiting imaginary frequencies, such as $\text{Ga}_{12}\text{N}_{12}$ -1D and $\text{Ga}_{16}\text{N}_{16}$ -1D/2D, were excluded from the optical analysis since they do not correspond to dynamically stable configurations [35].

This structural behavior differs from that reported for AlN [18] and MgS [19] nanostructures, which largely preserve their cubic-like symmetry even at larger sizes, reflecting a more rigid bonding framework. ScN systems exhibit intermediate behavior, maintaining structural stability while allowing greater geometrical variation [20].

The optical trends are also consistent with these comparisons. MgS nanostructures typically exhibit high-energy absorption onset and relatively sparse excitation spectra with weak geometry dependence, whereas ScN systems show lower-energy absorption and dense excitation patterns even at relatively small sizes. AlN nanostructures display intermediate behavior, combining moderate spectral broadening with greater structural preservation. In contrast, the optical response of $\text{Ga}_{16}\text{N}_{16}$ nanostructures is strongly morphology-dependent, with both the absorption onset and excitation distribution being highly sensitive to geometrical arrangement.

The observed symmetry reduction and structural reorganization of the $\text{Ga}_{16}\text{N}_{16}$ nanostructures differ from the behavior previously reported for AlN and MgS systems, which generally retain geometries closer to their original cubic-derived arrangements. This difference may be attributed to the larger atomic radius of Ga and the more flexible bonding environment in GaN nanostructures, which facilitate bond rearrangements during geometry optimization. As a result, the $\text{Ga}_{16}\text{N}_{16}$ clusters exhibit a stronger tendency toward structural distortion and the formation of partially hexagonal motifs. In contrast, the more rigid bonding frameworks of AlN and MgS nanostructures favor the preservation of their initial symmetry and structural organization. These observations suggest that both atomic size effects and bonding characteristics contribute to the distinct structural evolution observed in GaN nanostructures.

3.1.2. Structural Stabilization and Optical Response of $\text{Ga}_{24}\text{N}_{24}$ Nps

The second group of Ga_xN_x nanostructures examined in this study includes the $\text{Ga}_{24}\text{N}_{24}$ cluster and its structural variations (T-, S-, and F-type), as illustrated in Figure 3. Compared to the smaller systems, these nanostructures exhibit a more advanced stage of structural organization, characterized by increased compactness and the progressive formation of cage-like geometries [36].

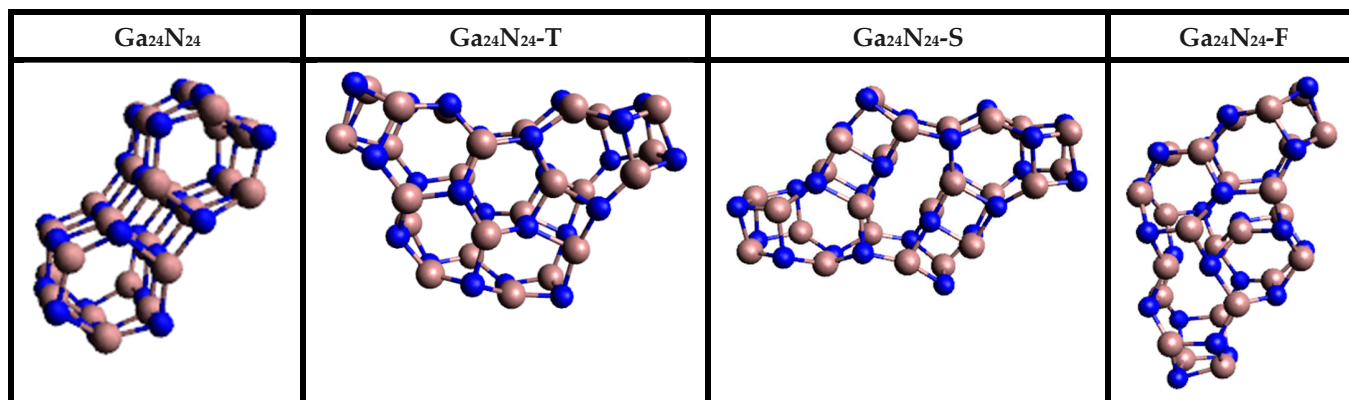


Figure 3. Optimized geometries of $\text{Ga}_{24}\text{N}_{24}$ nanostructures with different configurations (reference, T-, S-, and F-type), illustrating the formation of compact and cage-like arrangements. Gray spheres correspond to Ga atoms, while blue spheres represent N atoms.

The $\text{Ga}_{24}\text{N}_{24}$ systems represent an intermediate regime between smaller clusters and larger stabilized nanostructures, where the effects of size and morphology become more pronounced. The reference structure already exhibits a relatively closed geometry, while the T- and F-type configurations display more compact and symmetric arrangements. In contrast, the S-type structure presents a slightly more distorted bonding environment. A notable feature of this group is the increased presence of extended hexagonal-like motifs, indicating a progressive transition toward energetically favorable arrangements related to the hexagonal character of bulk GaN [37].

Figure 4 presents the optimized geometries reveal a clear structural evolution compared to the smaller Ga_8N_8 and $\text{Ga}_{16}\text{N}_{16}$ clusters. The T- and F-type structures adopt more compact and symmetric cage-like arrangements, whereas the S-type geometry retains a more distorted configuration. The increased structural organization and the development of extended hexagonal motifs indicate enhanced stabilization as the cluster size increases [36].

These structural differences are directly reflected in the optical properties of the $\text{Ga}_{24}\text{N}_{24}$ nanostructures. Compared to the $\text{Ga}_{16}\text{N}_{16}$ systems, the absorption spectra become broader and denser, extending approximately from 2.5 to 4.8 eV. A noticeable red-shift of the absorption onset is observed, indicating further reduction of the optical gap with increasing size. This behavior is associated with the larger cluster size and increased structural compactness, which favor stronger electronic delocalization and a higher density of accessible excited states.

Among the examined geometries, the T- and F-type configurations exhibit stronger absorption in the higher-energy region, whereas the S-type structure presents broader and more uniformly distributed spectral features. The reference structure shows intense peaks around 4.5–4.8 eV together with multiple lower-energy transitions, while the F-type geometry displays more localized peaks in the 3.5–4.3 eV region.

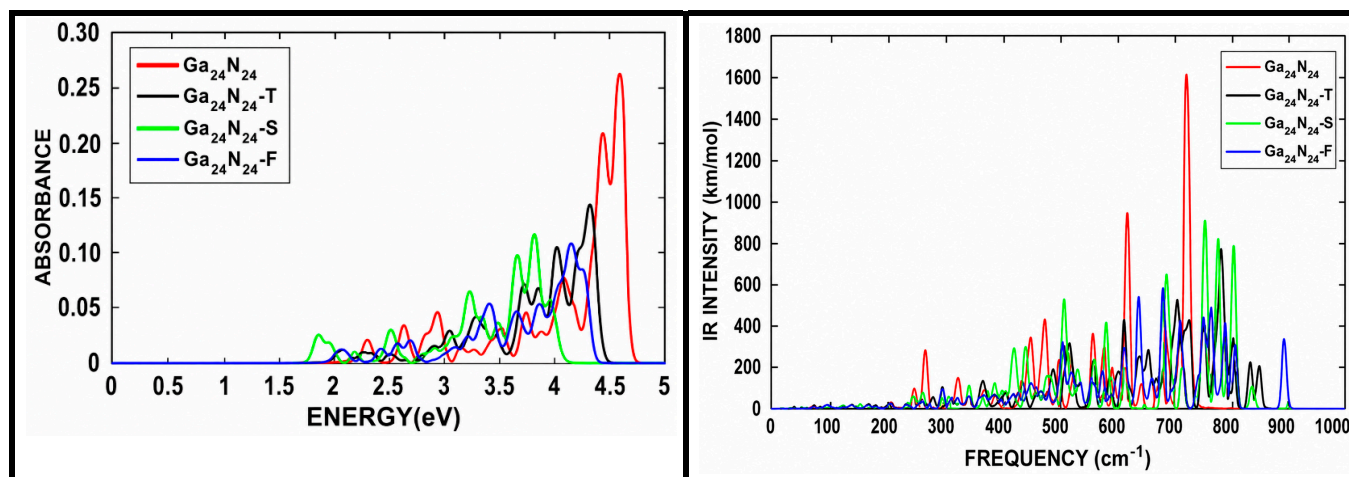


Figure 4. Calculated UV-Vis absorption and IR vibrational spectra of $\text{Ga}_{24}\text{N}_{24}$ nanostructures (reference, T-, S-, and F-type), illustrating the influence of size increase and structural reorganization on the electronic excitation behavior, spectral distribution, vibrational modes, and bonding environment of the examined configurations.

The vibrational spectra exhibit a similar increase in complexity. Compared to the smaller clusters, the $\text{Ga}_{24}\text{N}_{24}$ systems present a dense distribution of IR-active modes, mainly in the $650\text{--}800\text{ cm}^{-1}$ region, with intense peaks near $\sim 770\text{ cm}^{-1}$. The T- and F-type structures display sharper and more intense vibrational features, indicating increased structural rigidity and stronger Ga–N bonding interactions. In contrast, the S-type geometry exhibits a broader IR profile associated with its lower symmetry and more distorted bonding environment. In addition, the F-type structure presents a high-frequency mode near $\sim 930\text{ cm}^{-1}$, suggesting the presence of stiff localized bonding configurations [38].

Overall, the $\text{Ga}_{24}\text{N}_{24}$ nanostructures represent a transition regime between smaller distorted clusters and larger stabilized systems. The progressive formation of compact cage-like geometries and extended hexagonal motifs is accompanied by broader absorption spectra, lower optical onset energies, and richer vibrational fingerprints, demonstrating the strong coupling between structural organization and spectroscopic behavior.

This behavior differs from that reported for MgS nanostructures, which preserve relatively sparse absorption spectra with weak geometry dependence even at larger sizes. ScN systems exhibit similarly dense excitation spectra and low-energy absorption onset, although their optical response is generally less sensitive to morphology. AlN nanostructures display intermediate behavior, combining moderate spectral broadening with stronger preservation of structural symmetry [18–20].

Within the $\text{Ga}_{24}\text{N}_{24}$ family, morphology remains a key factor controlling the optical response. More compact configurations, such as the T- and F-type structures, exhibit stronger and more localized high-energy transitions, whereas the S-type geometry presents a more continuous excitation distribution across the spectrum.

3.1.3. Stability and Spectroscopic Properties of Hexagonal Ga_xN_x Nps

The third group of Ga_xN_x nanostructures examined in this study includes the explicitly constructed hexagonal Ga_6N_6 , $\text{Ga}_{12}\text{N}_{12}$, and $\text{Ga}_{18}\text{N}_{18}$ systems, as illustrated in Figure 5. In contrast to the previously analyzed cubic-derived configurations, these nanostructures were designed to represent well-defined hexagonal arrangements, enabling a direct investigation of symmetry-driven structural and spectroscopic behavior.

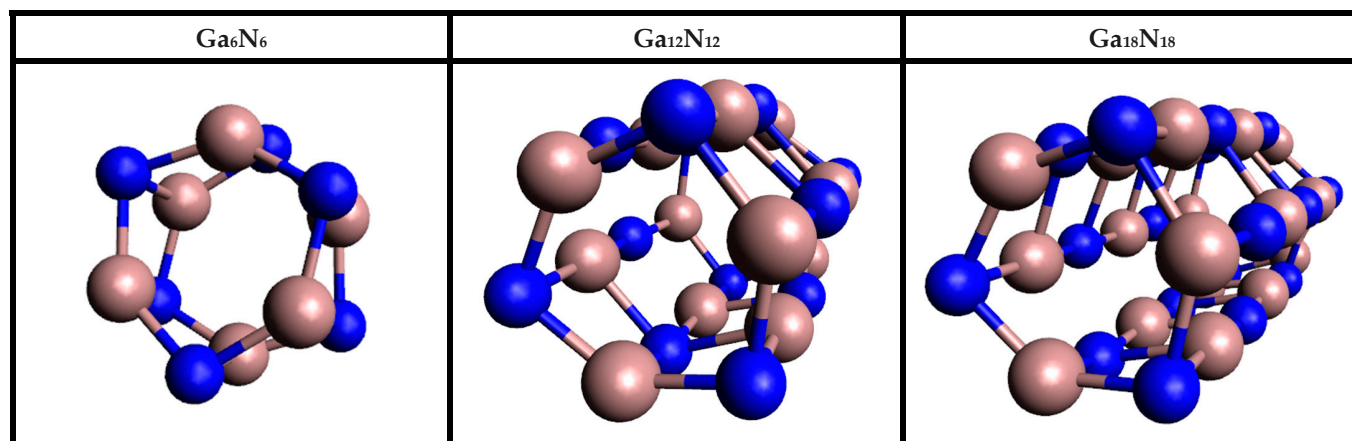


Figure 5. Optimized geometries of hexagonal Ga_6N_6 , $\text{Ga}_{12}\text{N}_{12}$, and $\text{Ga}_{18}\text{N}_{18}$ nanostructures, illustrating the development of hexagonal symmetry and extended bonding networks. Gray spheres correspond to Ga atoms, while blue spheres represent N atoms.

As the cluster size increases from Ga_6N_6 to $\text{Ga}_{18}\text{N}_{18}$, the geometries become progressively more ordered and structurally coherent, exhibiting extended bonding networks and enhanced symmetry. This evolution reflects the intrinsic preference of GaN systems for hexagonal coordination, consistent with the wurtzite structure of bulk GaN [6,7].

The optimized hexagonal structures exhibit a higher degree of symmetry compared to the cubic-derived geometries discussed previously, as shown in Figure 6. The Ga_6N_6 system already presents a well-defined hexagonal arrangement, while the larger $\text{Ga}_{12}\text{N}_{12}$ and $\text{Ga}_{18}\text{N}_{18}$ nanostructures exhibit increasingly extended and uniform bonding networks. The progressive increase in structural ordering indicates enhanced stabilization with increasing size [34].

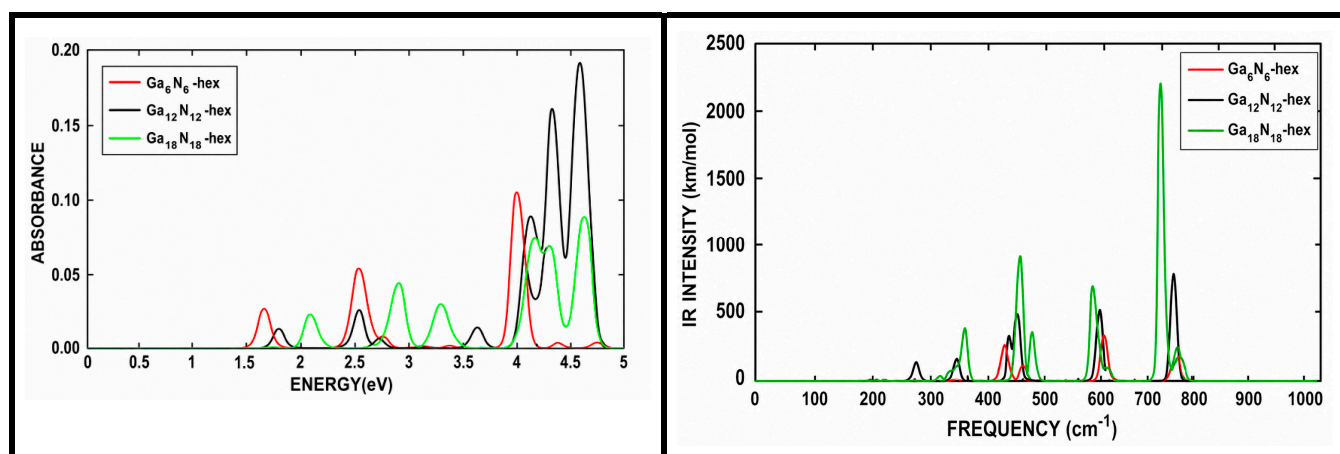


Figure 6. Calculated UV–Vis absorption and IR vibrational spectra of hexagonal Ga_6N_6 , $\text{Ga}_{12}\text{N}_{12}$, and $\text{Ga}_{18}\text{N}_{18}$ nanostructures, illustrating the evolution of electronic transitions, vibrational modes, and symmetry-dependent bonding characteristics with increasing cluster size.

The optical response of the hexagonal nanostructures differs significantly from that of the distorted cubic-derived systems. The absorption spectrum is characterized by relatively sharp and well-defined features, particularly in the high-energy region. The Ga_6N_6 structure exhibits a dominant peak around 4.3–4.4 eV, while the $\text{Ga}_{12}\text{N}_{12}$ system shows enhanced absorption in the 4.3–4.6 eV range. For the larger $\text{Ga}_{18}\text{N}_{18}$ nanostructure, the spectrum becomes moderately broader, with strong transitions extending approximately from 4.2 to 4.7 eV.

Compared to the cubic-derived GaN nanostructures, the hexagonal systems exhibit less fragmented spectra and larger separations between excitation peaks, indicating a more uniform electronic-state distribution and reduced spectral complexity [37]. The absorption onset also shifts toward higher energies, typically in the 4.2–4.5 eV region, suggesting larger optical gaps associated with the increased structural symmetry.

The vibrational spectra provide further evidence of the enhanced structural stability of the hexagonal configurations. In comparison with the distorted geometries, the IR spectra contain fewer but more intense vibrational modes. The Ga_6N_6 structure exhibits dominant peaks in the $600\text{--}700\text{ cm}^{-1}$ region, while the $\text{Ga}_{12}\text{N}_{12}$ and $\text{Ga}_{18}\text{N}_{18}$ systems display increasingly intense modes extending approximately up to $800\text{--}850\text{ cm}^{-1}$, indicating stronger Ga–N bonding interactions and increased structural rigidity [16]. The relatively narrow vibrational distributions reflect the reduced structural strain and higher symmetry of the hexagonal arrangements.

Overall, the combined structural and spectroscopic analysis demonstrates that the explicitly constructed hexagonal nanostructures represent highly stable and ordered configurations for GaN systems. Their well-defined optical and vibrational characteristics indicate that structural symmetry plays a dominant role in shaping the spectroscopic behavior of GaN nanostructures.

This behavior resembles that observed in MgS and AlN systems, which also exhibit relatively sparse excitation spectra and higher-energy absorption onset due to their strong structural symmetry. In contrast, ScN nanostructures maintain dense excitation spectra and lower-energy optical transitions even in more symmetric configurations [18–20].

As the size increases from Ga_6N_6 to $\text{Ga}_{18}\text{N}_{18}$, a moderate increase in spectral broadening is observed, although the overall spectral profiles remain significantly more organized than those of the distorted cubic-derived systems.

3.1.4. Dynamical Instability and Structural Reorganization in Low-Dimensional Ga_xN_x Systems

The final group of Ga_xN_x nanostructures examined in this study includes the low-dimensional and larger-scale systems $\text{Ga}_{12}\text{N}_{12}\text{--}1\text{D}$, $\text{Ga}_{16}\text{N}_{16}\text{--}1\text{D}$, $\text{Ga}_{16}\text{N}_{16}\text{--}2\text{D}$, $\text{Ga}_{32}\text{N}_{32}\text{--}2\text{DH}$, and $\text{Ga}_{36}\text{N}_{36}$, as illustrated in Figure 7. In contrast to the previously discussed compact and symmetric configurations, these systems were designed to investigate the effects of reduced dimensionality and increased cluster size on the structural behavior of GaN nanostructures [33].

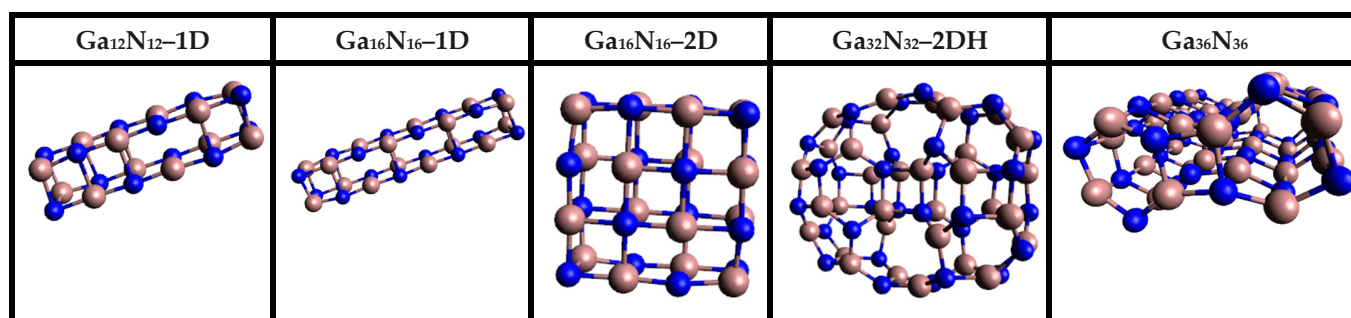


Figure 7. Optimized geometries of low-dimensional and larger-scale Ga_xN_x nanostructures ($\text{Ga}_{12}\text{N}_{12}\text{--}1\text{D}$, $\text{Ga}_{16}\text{N}_{16}\text{--}1\text{D}$, $\text{Ga}_{16}\text{N}_{16}\text{--}2\text{D}$, $\text{Ga}_{32}\text{N}_{32}\text{--}2\text{DH}$, and $\text{Ga}_{36}\text{N}_{36}$), illustrating the effect of dimensionality and size on structural organization. Gray spheres correspond to Ga atoms, while blue spheres represent N atoms.

The one-dimensional and two-dimensional configurations represent elongated and planar geometries that provide insight into the stability limits of low-dimensional GaN

arrangements. The larger systems extend this investigation toward more complex nanostructures, where structural reorganization and size-driven stabilization become increasingly important [35].

Structural visualization and analysis were performed using Avogadro. Due to the presence of dynamical instabilities in several configurations, the discussion is focused primarily on their structural characteristics and stability behavior.

The optimized geometries of the elongated $\text{Ga}_{12}\text{N}_{12}$ -1D, $\text{Ga}_{16}\text{N}_{16}$ -1D, and $\text{Ga}_{16}\text{N}_{16}$ -2D structures exhibit significant distortions, incomplete bonding networks, and pronounced deviations from symmetric arrangements. These features are directly associated with the presence of imaginary vibrational frequencies, indicating that the corresponding geometries do not represent true minima on the potential energy surface and are therefore dynamically unstable.

The instability of these low-dimensional configurations originates from the inability of elongated geometries to support a stable bonding environment in GaN systems. In contrast to hexagonal arrangements, the 1D and 2D structures introduce significant strain and under-coordination, leading to structural relaxation tendencies that cannot be fully accommodated within the imposed geometrical constraints. This behavior is consistent with the known preference of GaN for hexagonal (wurtzite-like) coordination [34].

Due to their dynamical instability, reliable optical and vibrational spectra were not obtained for the $\text{Ga}_{12}\text{N}_{12}$ -1D, $\text{Ga}_{16}\text{N}_{16}$ -1D, and $\text{Ga}_{16}\text{N}_{16}$ -2D systems. Consequently, these structures were excluded from the main spectroscopic analysis and considered only in the context of structural stability [35].

The larger $\text{Ga}_{32}\text{N}_{32}$ -2DH and $\text{Ga}_{36}\text{N}_{36}$ nanostructures exhibit markedly different behavior. Both systems evolve toward compact cage-like geometries with partial hexagonal ordering [35,36], suggesting enhanced stabilization with increasing size. Previous theoretical studies have similarly identified GaN nanocages as energetically favorable structural motifs with distinctive electronic and optical properties [36], supporting the structural evolution observed in the present work. In particular, the $\text{Ga}_{32}\text{N}_{32}$ -2DH structure presents a highly organized arrangement consistent with its large binding energy, while the $\text{Ga}_{36}\text{N}_{36}$ configuration retains a compact morphology despite the presence of moderate structural distortions.

Based on the trends observed for the smaller stable clusters, these larger systems are expected to exhibit lower absorption onset energies together with dense excitation spectra, indicating increased electronic delocalization and a gradual transition toward bulk-like optical behavior.

This behavior differs from that observed in MgS and AlN systems, where elongated configurations can remain structurally stable due to stronger ionic bonding and higher structural rigidity. ScN systems also exhibit greater tolerance toward low-dimensional geometries, maintaining stability across a wider range of configurations [18–20]. In contrast, GaN nanostructures remain strongly sensitive to morphology, highlighting the critical role of geometry in determining both structural stability and spectroscopic behavior.

3.2. Stability and Binding Energy

To quantitatively evaluate the energetic stability of the optimized Ga_xN_x NPs, the binding energy (BE) per formula unit (f.u.) was calculated using both self-consistent field (SCF) energies and zero-point vibrational energy (ZPE)-corrected values. It should be noted that the binding energies reported here are referenced to isolated Ga and N atoms in order to ensure internal consistency among different cluster geometries. Although this convention may overestimate absolute cohesive energies, it allows a reliable comparison of relative stability trends across the studied Ga_xN_x nanoparticles, including both cubic-

derived and hexagonal reference structures, as also followed in related studies on AlN-, ScN-, and MgS-based nanostructures [18–20].

The binding energy was calculated using the following expression:

$$E_B(\text{Ga}_x\text{N}_x) = xE(\text{Ga}) + xE(\text{N}) - E(\text{Ga}_x\text{N}_x)$$

where the index (x) denotes the number of GaN formula units in the examined nanostructure, $E(\text{Ga})$ is the energy of the isolated Ga atom, $E(\text{N})$ is the energy of the isolated N atom, and $E_B(\text{Ga}_x\text{N}_x)$ is the total energy of the corresponding nanoparticle. The binding energy per f.u., E_B , is then given by:

$$E_B(\text{Ga}_x\text{N}_x) = \frac{E_B(\text{Ga}_x\text{N}_x)}{x} = E(\text{Ga}) + E(\text{N}) - \frac{E(\text{Ga}_x\text{N}_x)}{x}$$

In addition to the SCF-based values, ZPE-corrected binding energies were also evaluated in order to assess the influence of vibrational contributions on the energetic ordering of the studied clusters. The resulting values are presented together with the corresponding HOMO–LUMO gaps in Table 2.

Table 2. HOMO–LUMO(HL) gaps and binding energies per f.u. of Ga_xN_x NPs.

Examined NPs	HL Gap (eV)	Binding Energy per f.u. (eV)	Binding Energy per f.u. with ZPE (eV)
Ga_8N_8	1.221	5.56	5.44
$\text{Ga}_6\text{N}_6\text{-Hex}$	1.778	6.17	6.04
$\text{Ga}_{12}\text{N}_{12}\text{-Hex}$	2.129	6.36	6.23
$\text{Ga}_{18}\text{N}_{18}\text{-Hex}$	2.333	6.50	6.36
$\text{Ga}_{16}\text{N}_{16}\text{-T}$	2.287	6.38	6.25
$\text{Ga}_{16}\text{N}_{16}\text{-S}$	2.493	6.42	6.28
$\text{Ga}_{16}\text{N}_{16}\text{-L}$	2.370	6.39	6.25
$\text{Ga}_{16}\text{N}_{16}\text{-L3}$	2.305	6.37	6.24
$\text{Ga}_{24}\text{N}_{24}$	2.250	6.52	6.39
$\text{Ga}_{24}\text{N}_{24}\text{-T}$	2.398	6.62	6.48
$\text{Ga}_{24}\text{N}_{24}\text{-S}$	2.040	6.45	6.32
$\text{Ga}_{24}\text{N}_{24}\text{-F}$	2.069	6.61	6.48
$\text{Ga}_{32}\text{N}_{32}\text{-2DH}$	2.964	6.90	—
$\text{Ga}_{36}\text{N}_{36}$	2.233	6.63	—

For $\text{Ga}_{32}\text{N}_{32}\text{-2DH}$ and $\text{Ga}_{36}\text{N}_{36}$, only SCF-based binding energies are reported because harmonic vibrational frequency calculations were not performed for these larger nanostructures due to their substantially increased computational cost. Consequently, ZPE-corrected binding energies are not available for these two systems.

As shown in Table 2, the binding energy per formula unit (BE/f.u.) and the ZPE-corrected BE/f.u. exhibit consistent trends across the entire set of Ga_xN_x nanostructures. In general, the BE/f.u. increases significantly from 5.56 eV for the Ga_8N_8 system to values in the range of 6.3–6.6 eV for medium- and large-sized nanostructures. More specifically, values of 6.38, 6.42, 6.39, and 6.37 eV were obtained for the $\text{Ga}_{16}\text{N}_{16}\text{-T}$, $\text{Ga}_{16}\text{N}_{16}\text{-S}$, $\text{Ga}_{16}\text{N}_{16}\text{-L}$, and $\text{Ga}_{16}\text{N}_{16}\text{-L3}$ geometries, respectively, while even higher values were found for the $\text{Ga}_{24}\text{N}_{24}$ -based systems, reaching 6.62 eV for $\text{Ga}_{24}\text{N}_{24}\text{-T}$ and 6.61 eV for $\text{Ga}_{24}\text{N}_{24}\text{-F}$. This

increase indicates that larger clusters are energetically favored, as more Ga–N bonds per formula unit contribute to the overall stabilization.

At the same time, the results reveal that geometry also plays an important role in the energetic stability. Among the $\text{Ga}_{16}\text{N}_{16}$ nanostructures, the S-shaped geometry exhibits the highest BE/f.u., suggesting a slightly more favorable local bonding environment compared to the T-, L-, and L3-type structures. Similarly, in the $\text{Ga}_{24}\text{N}_{24}$ series, the T and F geometries appear to be the most stable, while the S configuration yields the lowest BE/f.u. in this size regime. These differences, although relatively small, indicate that the energetic landscape is sensitive not only to size but also to structural arrangement and symmetry [38].

The explicitly examined hexagonal structures exhibit binding energies per formula unit of 6.17, 6.36, and 6.50 eV for Ga_6N_6 -Hex, $\text{Ga}_{12}\text{N}_{12}$ -Hex, and $\text{Ga}_{18}\text{N}_{18}$ -Hex, respectively. These results indicate a progressive increase in energetic stability with increasing cluster size within the hexagonal series [34,37]. The observed trend suggests that larger hexagonal nanostructures benefit from enhanced structural organization and more favorable Ga–N bonding interactions, leading to stronger overall stabilization. Furthermore, the binding energies of the hexagonal nanostructures are comparable to those of the cubic-derived configurations, indicating that hexagonal arrangements remain energetically competitive and physically meaningful structural motifs for GaN systems.

The additional structures $\text{Ga}_{32}\text{N}_{32}$ -2DH and $\text{Ga}_{36}\text{N}_{36}$, for which only SCF-based energies are available, further enrich the stability analysis. In particular, the $\text{Ga}_{32}\text{N}_{32}$ -2DH structure exhibits the highest BE/f.u. value of the whole series, equal to 6.90 eV, indicating a particularly favorable energetic stabilization. The $\text{Ga}_{36}\text{N}_{36}$ structure also remains highly stable, with a BE/f.u. value of 6.63 eV, comparable to those of the most stable $\text{Ga}_{24}\text{N}_{24}$ -based geometries. These results suggest that larger GaN nanostructures generally exhibit enhanced energetic stabilization, although the exact binding energy remains sensitive to geometry, dimensionality, and structural reorganization.

The unusually high binding energy of the $\text{Ga}_{32}\text{N}_{32}$ -2DH nanostructure may be attributed to its compact geometry and efficient bonding network, which maximize favorable Ga–N interactions per formula unit. This result suggests that structural organization can play an equally important role as cluster size in determining the energetic stability of Ga_xN_x nanostructures. The high binding energies obtained for both $\text{Ga}_{32}\text{N}_{32}$ -2DH and $\text{Ga}_{36}\text{N}_{36}$ further indicate that compact cage-like nanostructures remain energetically favorable at larger sizes. This behavior is consistent with the overall stability trend observed throughout the investigated Ga_xN_x series and suggests that increased structural organization and efficient bonding networks contribute significantly to the stabilization of larger nanostructures.

ZPE corrections uniformly reduce the BE/f.u. values by approximately 0.12–0.14 eV per formula unit across all systems for which vibrational corrections were available. Despite this reduction, the energetic ordering of the nanostructures remains essentially unchanged, confirming the robustness of the observed stability trends. The close agreement between corrected and uncorrected values further supports the validity of using BE/f.u. as a reliable descriptor of relative stability in Ga_xN_x nanoparticles.

In order to better visualize the evolution of the energetic stability across the investigated Ga_xN_x nanostructures, the calculated binding energies per formula unit (BE/f.u.), together with their ZPE-corrected values, are plotted as a function of nanoparticle size and geometry in Figure 8. This graphical representation complements the numerical values listed in Table 2 and allows a clearer comparison of the stability trends among cubic-derived, asymmetric, and hexagonal configurations.

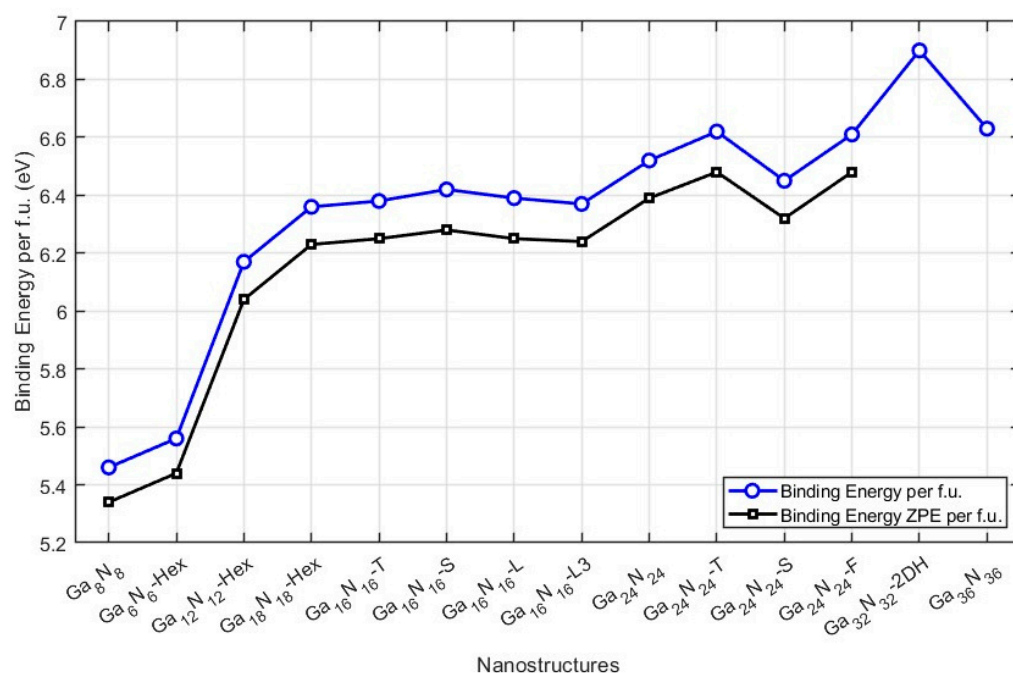


Figure 8. Total binding energies per formula unit (blue markers) and ZPE-corrected binding energies per formula unit (black markers) for all Ga_xN_x nanostructures investigated in this work, plotted as a function of nanoparticle size and geometry. Each data point corresponds to an optimized cluster of formula Ga_xN_x , including cubic-derived, asymmetric, and hexagonal configurations.

As shown in Figure 8, the binding energy per formula unit follows a clear overall increasing trend with cluster size, indicating progressive stabilization of the Ga_xN_x nanostructures as the number of Ga–N bonds increases. The most pronounced increase is observed in the transition from the smallest clusters to the intermediate-sized systems, while for larger nanostructures the energetic variation becomes more moderate, suggesting a tendency toward stabilization saturation. In addition, the diagram clearly reveals the effect of geometry on the energetic ordering, since structures with the same stoichiometry may exhibit small but noticeable differences in BE/f.u. depending on their morphology. The ZPE-corrected values remain systematically lower than the corresponding SCF-based energies, but they follow the same overall trend, confirming that the relative stability ordering is preserved.

The inclusion of $\text{Ga}_{32}\text{N}_{32}$ -2DH and $\text{Ga}_{36}\text{N}_{36}$ in the SCF curve further strengthens this analysis. In particular, the $\text{Ga}_{32}\text{N}_{32}$ -2DH structure exhibits the highest BE/f.u. value among all investigated systems, suggesting a highly favorable energetic stabilization. In contrast, the $\text{Ga}_{36}\text{N}_{36}$ structure, although still highly stable, presents a slightly lower BE/f.u., indicating that the stabilization trend does not evolve strictly monotonically with size, but is also influenced by the specific geometry and structural reorganization of the nanocluster [32,33].

Overall, Figure 8 reinforces the conclusion that the energetic stabilization of Ga_xN_x nanostructures is not governed solely by size, but also by geometry, with hexagonal and compact configurations emerging as particularly favorable. In particular, the enhanced stability of the $\text{Ga}_{32}\text{N}_{32}$ -2DH structure suggests that structural reorganization toward more compact and energetically optimized motifs may play a decisive role in the evolution of larger GaN nanoclusters.

4. Conclusions

In this work, the structural, electronic, optical, and vibrational properties of a series of Ga_xN_x nanostructures were systematically investigated using DFT and TD-DFT calculations. Benchmark calculations on the Ga_4N_4 cluster demonstrated that the CAM-B3LYP functional provides excitation energies in good agreement with high-level EOM-CCSD results, while B3LYP ensures reliable geometries and vibrational stability.

The obtained results reveal a strong dependence of the structural and spectroscopic behavior of Ga_xN_x nanostructures on size, geometry, and dimensionality. The smaller Ga_8N_8 cluster retains a compact and highly symmetric cubic-like geometry, whereas the larger $\text{Ga}_{16}\text{N}_{16}$ and $\text{Ga}_{24}\text{N}_{24}$ systems exhibit progressively reduced symmetry, broader absorption spectra, and richer vibrational fingerprints. Increasing cluster size also promotes structural reorganization toward more compact and cage-like arrangements.

The explicitly constructed hexagonal Ga_6N_6 , $\text{Ga}_{12}\text{N}_{12}$, and $\text{Ga}_{18}\text{N}_{18}$ nanostructures exhibit enhanced structural ordering and well-defined spectroscopic features, confirming the intrinsic tendency of GaN systems toward hexagonal coordination related to the wurtzite phase of bulk GaN. In contrast, elongated low-dimensional configurations such as $\text{Ga}_{12}\text{N}_{12}$ -1D, $\text{Ga}_{16}\text{N}_{16}$ -1D, and $\text{Ga}_{16}\text{N}_{16}$ -2D were found to be dynamically unstable due to the presence of imaginary vibrational frequencies associated with structural strain and incomplete bonding environments.

The larger $\text{Ga}_{32}\text{N}_{32}$ -2DH and $\text{Ga}_{36}\text{N}_{36}$ nanostructures further demonstrate the tendency of GaN systems to evolve toward compact three-dimensional geometries with partial hexagonal ordering. Overall, the results indicate that structural organization plays a decisive role in determining the optical and vibrational behavior of Ga_xN_x nanostructures.

Comparison with previously studied AlN, ScN, and MgS nanostructures highlights the distinctive behavior of GaN systems, which combine strong geometry-dependent optical response with significant structural flexibility. These findings provide useful insight into the relationship between structure and optoelectronic properties in semiconductor nanoclusters and may contribute to the rational design of GaN-based nanoscale optoelectronic materials.

Future work may include the investigation of larger GaN nanostructures and the incorporation of environmental effects, such as substrate interactions and temperature-dependent behavior, in order to further explore the evolution of their optoelectronic properties.

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