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Size-dependence of the Linear and Nonlinear Optical Properties of GaN Nanoclusters

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ABSTRACT

In this paper, we present the results of our first-principles quantum mechanical studies of the electronic structure, geometry, and linear and nonlinear optical (NLO) properties of tetrahedral Ga_mN_m (m=1, 4, 7, 17) atomic clusters. Our calculated results suggest that the linear and NLO properties both exhibit a strong dependence upon cluster size and shape (geometry). However, the size- and the geometry-dependences are more pronounced for the NLO properties than for the linear optical properties. For clusters containing equal numbers of Ga and N atoms, an open-structure with no network-forming ring has a much larger second-order NLO coefficient than a cluster with a closed ring structure.

INTRODUCTION

The linear and nonlinear optical properties of III-V binary semiconductors have been the subject of active research since the late 1960s [1,2]. Recent advancements in (a) experimental techniques to fabricate/produce stable isolated nanometer-size binary atomic clusters composed of group III and group V elements and (b) techniques and tools to probe response properties of nanoscale objects, have attracted a great deal of attention to the linear and nonlinear optical properties of III-V nanoclusters due to their potential applications in future communications technologies [3]. An important issue in a bottom-up approach to fabricating nanoclusters for future technological applications is an understanding of the evolution of their response properties with cluster size and shape. Theoretical work on atomic clusters of III-V semiconductors have examined the electronic structure and stability of small clusters using density functional theory [4,5] and their linear and non-linear optical properties using the *ab initio* time dependent Hartree-Fock formalism [6,7,8] as well as time-dependent density functional theory [9]. Work by Kandalam et al. suggests that as cluster sizes increase a transition from low energy planar to bulk-like 3-D structures occurs in some nitrides [4]. As non-linear optical properties of molecules are particularly sensitive to their 3-D structure, this suggests a strong dependence of the NLO properties on cluster size. Indeed, work by Natarajan et al. on the atomic and electronic structures of IV-VI semiconductor structures (Ge_mTe_n, $m+n \leq 10$) suggest that the polarizabilities of the clusters vary non-monotonically with cluster size [10].

In order to better understand the dependence of optical properties on geometrical structure, we have undertaken a systematic study of the electronic and geometrical structures and the optical properties of stable GaN nanoclusters. We present an *ab initio* time-dependent Hartree-Fock (TDHF) study of the (hyper)polarizabilities of three-dimensional Ga_mN_m (m=1,4,7,17) clusters with bulk-like bonding. The technical details of the calculations are discussed in the first section. We then present the results for both linear and non-linear properties. Issues relating to cluster size and shape, such as approach to the bulk limit, are discussed.

CALCULATIONAL DETAILS

All optical property calculations were performed on Ga_mN_mclusters using the GAMESS electronic structure package [11]. Surface hydrogens were added to the clusters in order to eliminate surface electronic effects by terminating dangling bonds. The geometrical structures of the clusters were optimized at the *ab initio* Hartree-Fock level using a large polarized basis set, DZP(1*p*,1*d*), as well as Stevens-Basch-Krauss-Jasien-Cundari (SBKJC) effective core potentials [12] for the Ga and N atoms. The exponents of the basis sets employed are the defaults in GAMESS. The components of the polarizability and the 1st hyper-polarizability tensors were computed using the time-dependent Hartree-Fock (TDHF) method [13] using the same DZP basis set as used for the geometry calculation. The orientationally averaged linear polarizability $<\alpha(\omega)>$ is presented for the static limit ω=0 as well as the optical wavelength of λ= 1064nm. The hyperpolarizability tensors corresponding to the electroptic Pockels effect (EOPE), $\beta(-\omega;0,\omega)$, second harmonic generation (SHG),$\beta(-2\omega;\omega,\omega)$, and optical rectification (OR), $\beta(0;\omega,-\omega)$, were computed at λ= 1064nm.

The sensitivity of the optical properties to the computed geometry was studied by comparing the properties of clusters optimized with SBKJC and DZP(1*p*,1*d*) basis sets. The convergence of the optical properties with respect to basis set size (including number of polarization functions employed) on the calculated optical properties was also studied by recomputing the properties of the DZP(1*p*,1*d*) structures with additional *p, d*, and *f* polarization functions.

RESULTS

Figures 1 and 2 show the clusters employed in this study arranged in order of increasingly bulk-like character. The bonding in these clusters is generally tetrahedral. The clusters in Figure 1 are what we term "open" in the sense that they do not contain ring structures. By contrast, the clusters in Figure 2 are composed of "closed" network-forming rings. The clusters in Figure 1 were taken from Korambath et al.[7] who employed an even-tempered Gaussian (ETG) basis set for their calculations on clusters up through *m*=4. The Ga_4N_4 clusters, Figure 1(B) and Figure 2(A), are related in that they represent the simplest open and closes GaN structures that can be carved out of a periodic arrangement of GaN atoms like that in Figure 2(C). They were chosen to provide insight into the effect that small changes in atomic arrangements can have on optical properties.

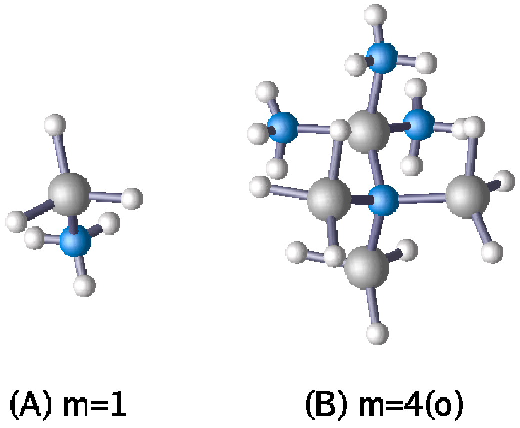

Figure 1. Open GaN structures: (A) $GaNH_6$ and (B) $Ga_4N_4H_{18}$. Nitrogen atoms are shown in blue, gallium in silver and hydrogen in white.

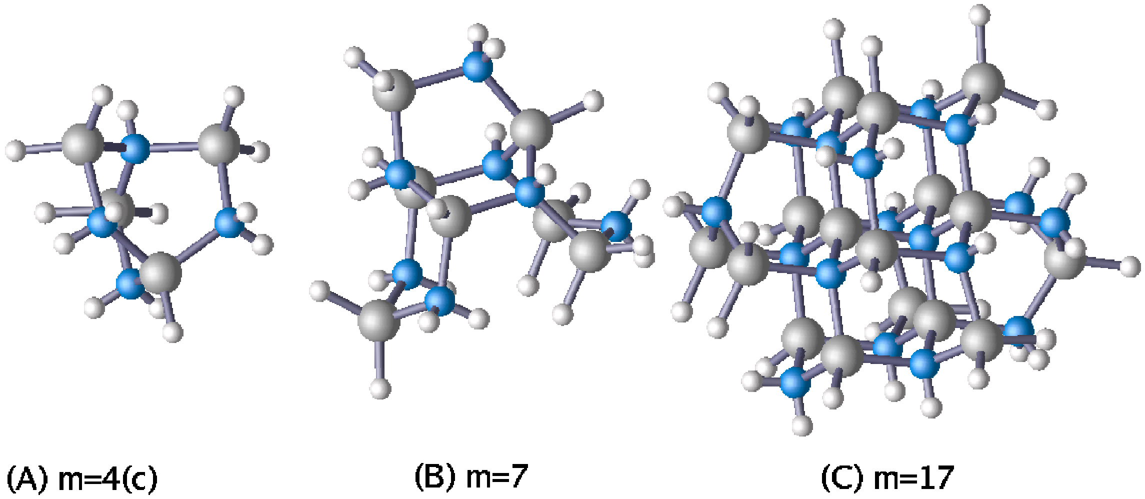

Figure 2. Closed GaN structures: (A) $Ga_4N_4H_{14}$, (B) $Ga_7N_7H_{22}$, and (C) $Ga_{17}N_{17}H_{38}$. Nitrogen atoms are shown in blue, gallium in silver and hydrogen in white.

Linear Optical Properties

Table I shows the calculated dipole moments of the clusters as a function of basis set size. The calculated dipole moment appears to be reasonably well converged even for the smallest basis set. The magnitudes of the computed dipole moments are not well correlated with cluster size, but are more generally related to the overall symmetry of the cluster.

Table I. Dipole moments in Debye for optimized clusters computed at the DZP(1*p*,1*d*) geometry as a function of basis set size.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	5.21	5.15	5.15
4(o)	18.60	18.34	18.34
4(c)	5.92	5.80	5.80
7	2.66	2.62	2.62
17	13.19	-	-

Tables II and III show the variation of the isotropically-averaged static and frequency dependent polarizabilities as functions of cluster size and the basis set employed in the properties calculation. Polarizabilities for basis sets larger than DZP(1*p*,1*d*) for the *m*=17 cluster were not computed owing to the large computational requirements. However, we can still draw conclusions from the trends in the data since (1) the polarizabilities were generally found to be well-converged at the DZP(3*p*, 3*d*) level and (2) the relative differences between results of the relatively inexpensive DZP(1*p*,1*d*) polarizability calculations and the results of the more expensive calculations rapidly decrease from 14% to 7% as *m* increases from 1 to 7. This suggests that the computed value of the linear polarizability computed at the DZP(1*p*,1*d*) level for *m*=17 should be a reasonable estimate of the polarizability one would obtain from a larger calculation.

Table II. Isotropically-averaged static polarizability, $\alpha(0)$ (10^{-24} cm^3), as a function of basis set at the DZP(1*p*,1*d*) geometry. The final column gives our best value for the polarizability per GaN unit.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**	**$\alpha(0)/m$**
1	5.38	6.26	6.26	6.26
4(o)	20.00	22.34	22.35	5.59
4(c)	17.68	19.25	19.25	4.81
7	29.79	31.93	31.94	4.56
17	63.97	-	-	3.76

Table III. Isotropically-averaged frequency dependent polarizability, α(ω) (10^{-24} cm^3 ≡ 10^{-24} esu^2 cm^2 erg^{-1}) at λ = 1064nm, as a function of basis set at the DZP(1*p*,1*d*) geometry. The final column gives our best value for the polarizability per GaN unit.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**	**α(ω)/*m***
1	5.42	6.32	6.32	6.32
4(o)	20.18	22.58	22.59	5.65
4(c)	17.83	19.43	19.44	4.86
7	30.03	32.22	32.23	4.60
17	64.48	-	-	3.79

The values we compute for the dipole moments and linear polarizabilities for *m*=1 and 4(o) are in rough agreement with the results obtained by Korambath et al. [7] who noted that the polarizability of clusters depended in an approximately linear fashion on the number of GaN units in the cluster. Our value for the polarizability per GaN unit is slightly larger however. In the final columns of Tables II and III, we compute the polarizability per GaN unit using our best available value for each cluster. Our results suggest that the polarizability per GaN unit slowly decreases with cluster size and that it may already be near the bulk limit (~3.2-3.9 x 10^{-24} cm^3) by *m*=17.[15]

The apparent convergence toward the bulk limit observed in the polarizability is not seen in other properties. Table IV shows the trends in energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as a function of basis set and the sizes of our clusters. It is expected that this quantity should decrease as a function of cluster size, and in the bulk limit approach the band gap of the crystalline material. Table IV suggests that this approach to the bulk limit is slow and depends on the shape of the cluster in a non-trivial fashion.

Table IV. HOMO-LUMO energy differences in eV as a function of basis set for optimized clusters at the DZP(1*p*,1*d*) geometry.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	13.58	11.99	11.99
4(o)	10.85	9.13	9.13
4(c)	13.03	11.21	11.21
7	13.41	11.86	11.86
17	11.64	-	-

Non-linear optical properties

The first hyperpolarizability, $\beta=\beta(-\omega_\sigma;\omega_1,\omega_2)$ is a rank 3 tensor quantity, and depends upon the symmetry of the atomic system studied. For centrosymmetric systems, β vanishes. When β is non-zero, a vector component β_μ, directed along the applied electric field, is usually observed. A related and frequently reported theoretical quantity is

$$\beta_{vec} = \sqrt{\left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)} \qquad (2)$$

where the β_i ($i = x, y, z$) are determined from the tensor components, β_{ijk}, of $\boldsymbol{\beta}$ as

$$\beta_i = \frac{1}{3}\sum_{j=x,y,z}\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right). \qquad (3)$$

The former quantity (Eq. 2) evaluated for frequencies corresponding to the static hyperpolarizability, the electroptic Pockels effect, and second harmonic generation is shown in Tables V-VIII. The calculated values have also been divided by a factor of 2 so that the values we report are consistent with the conventions found in the experimental literature instead of those in the quantum chemical literature [14].

Tables V and VI show the effect of the basis set used for the geometry optimization as well as the basis set used on the NLO properties on the static hyperpolarizabilities, β(0;0,0), computed for our clusters. As was seen in the calculation of the linear polarizabilities, the smallest basis set results are not completely converged. From tables V and VI we see that the geometry used in the calculation (SBKJC or DZP) has a weak effect on the computed hyperpolarizability.

Table V. Static hyperpolarizability, β(0;0,0), of the clusters in 10^{-32} esu^3 cm^3 erg^{-2} as a function of basis set at SBKJC optimized geometry.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	30.87	31.89	32.05
4(c)	5.80	14.15	13.99
7	44.75	38.15	37.99
17	119.27	-	-

Table VI. Static hyperpolarizability, β(0;0,0), of the clusters in 10^{-32} esu^3 cm^3 erg^{-2} as a function of basis set at the DZP(1*p*,1*d*) optimized geometry.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	27.16	29.43	29.61
4(o)	153.83	89.97	90.94
4(c)	0.93	11.93	11.74
7	32.29	33.59	33.32
17	116.14	-	-

Table VII. EOPE hyperpolarizability, β(-ω;0,ω), of clusters in 10^{-32} esu^3 cm^3 erg^{-2} at λ = 1064nm as a function of basis set using DZP(1*p*,1*d*) optimized geometry. The results for OR (optical rectification), β(0;-ω,ω) are identical.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	27.71	30.17	30.35
4 (o)	158.67	95.01	96.02
4 (c)	1.05	12.18	11.99
7	33.08	34.21	33.93
17	119.93	-	-

Table VIII. Second harmonic generation hyperpolarizability, β(-2ω; ω, ω), of clusters in 10^{-32} esu^3 cm^3 erg^{-2} at λ = 1064nm as a function of basis set using DZP(1*p*,1*d*) optimized geometry.

***m*, Ga$_m$N$_m$**	**DZP(1*p*,1*d*)**	**DZP(3*p*,3*d*)**	**DZP(3*p*,3*d*,1*f*)**
1	28.87	31.72	31.91
4(o)	169.15	106.89	107.98
4(c)	1.31	12.68	12.48
7	34.76	35.47	35.16
17	128.10	-	-

Tables VI – VIII show that the variation of hyperpolarizabilities with cluster size and shape are pronounced, but perhaps not as large as suggested by the previous results of Korambath, et al. who computed hyperpolarizabilities for *m*=4(o) that are more than twice what we found. The hyperpolarizabilities in our study vary over roughly an order of magnitude and appear to be strongly correlated with both the size of the clusters and degree of compactness of the cluster shapes. These size and shape effects can either reinforce one another or cancel. This correlation suggests that experimentally observed hyperpolarizabilities will exhibit oscillatory behavior as a function of cluster size. The degree of oscillation will depend upon the relative stabilities of the various possible shapes of a cluster of a given size and their point symmetry. The magnitudes of the various second-order effects show the expected trend of β(-2ω; ω, ω) > β(-ω;0,ω) > β(0;0,0) as was reported previously [7].

SUMMARY

We have calculated the (hyper)polarizabilites of a series of Ga$_m$N$_m$ clusters of varying size and shape. The convergence of these properties with respect to basis set size was studied and found to be well converged at the DZP(3*p*, 3*d*) level. Our results also suggest that the number of polarization functions included in the calculation becomes less important for larger clusters. The linear polarizability of a GaN unit in a cluster is found to slowly vary with cluster size and appears to quickly approach the bulk value of 3.9 $Å^3$. The linear polarizability exhibits small frequency dispersion. Other properties appear to converge more slowly with cluster size.

The hyperpolarizabilities are found to oscillate strongly with cluster size owing to competing size and shape effects. For equal numbers of Ga and N atoms (e.g., Ga_4N_4), the structure with reduced symmetry gives a substantially enhanced value of β as compared with the more symmetric structure. As the range of energetically accessible structures depends upon temperature, this suggests that the variation of hyperpolarizabilities with cluster size will depend strongly on temperature.

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