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(Hyper)polarizabilities of GaN, GaP, and GaAs Clusters: An Ab Initio Time-Dependent Hartree−Fock Study[†]

Prakashan P. Korambath* and Shashi P. Karna*

Space Vehicles Directorate, Air Force Research Laboratory, 3550 Aberdeen Avenue SE,
Building 914, Kirtland Air Force Base, New Mexico 87117-5776

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The (hyper)polarizabilities of GaN, GaP, and GaAs clusters have been calculated using an ab initio time-dependent Hartree−Fock method and an even-tempered Gaussian basis set. The geometries of the clusters used in the study were optimized by ab initio Hartree−Fock calculations using the same basis set. The clusters used in this calculation are of the type Ga_mX_n ($m = 1, 3, 4$ and $n = 1, 3, 4$) where X = N, P, or As. The Ga_mX_n clusters are in a charge neutral ($q = 0$) state for $m = n$ and in an appropriately charged state for $m \neq n$. All of the clusters studied are stable in a nearly tetrahedral geometry. The magnitude of the calculated (hyper)polarizabilities appears to depend on the size of the cluster. The cluster-size dependence of calculated (hyper)polarizabilities is more pronounced for the first hyperpolarizability, β, than for the polarizability, α. The calculated frequency-dependent polarizability, $\alpha(\omega)$, exhibits a small but finite dispersion with the frequency of the optical field. The magnitude of the calculated $\beta(-\omega_\sigma;\omega_1,\omega_2)$ corresponding to various second-order effects shows the expected trend of $\beta(-2\omega;\omega,\omega) > \beta(-\omega;0,\omega) > \beta(0;0,0)$.

I. Introduction

The binary semiconductor materials composed of group III−V elements have a wide range of technological applications.[1] Interest in the nonlinear optical (NLO) properties of the group III−V binary semiconductors dates back to the late 1960s when Levine[2] predicted that GaN crystals would possess large second-order nonlinearity in both the zinc blende and wurtzite forms. In fact, the second-order NLO susceptibility of GaN crystals was found to be comparable to that of the conventional nonlinear crystals such as potassium dihydrogen phosphate (KDP).[3,4] Since then, there have been several experimental[5,6] and theoretical[7] studies on the NLO properties of group III−V binary materials. Recent advances in experimental techniques to synthesize and analyze stable clusters composed of group III−V elements have generated a great deal of interest in the NLO properties of these chemically engineered species.[8−10] Very recently, Schlecht et al.[11] and Schäfer et al.[12] have reported the electric dipole polarizability of isolated GaAs clusters. It has been suggested that impurities and defects[13] can have a significant effect on the optical nonlinearities of these materials. Therefore, an understanding of the basic mechanism of NLO response and its relationship with the microscopic features of group III−V clusters is considered important and timely. Previous theoretical calculations[7] of the NLO properties of group III−V semiconductors have been focused on the bulk susceptibilities for periodic lattice systems.

The goal of the present work is to develop a theoretical understanding of the microscopic electrooptic properties of Ga_mX_n (X = N, P, As) clusters relevant to crystalline state and thin films as used in various devices. We present here an ab initio time-dependent Hartree−Fock (TDHF) study of the (hyper)polarizabilities of small to medium size Ga_mX_n ($m = 1, 3, 4$; $n = 1, 3, 4$) clusters. NLO properties have been calculated for Ga_mX_n clusters in *tetrahedral* geometry optimized via ab initio Hartree−Fock (HF) calculations. The effects of the type and the number of heteroatoms on the (hyper)polarizabilities of the clusters are investigated and discussed.

Technical details of the theoretical calculations are discussed in section II. Calculated results for the Ga_mX_n clusters are presented and discussed in section III. The main findings of the study are summarized in section IV.

II. Technical Details of Calculations

The geometry optimization was performed at the ab initio HF level of theory using an even-tempered Gaussian (ETG)[14] basis set. The clusters used in this study have a nearly tetrahedral optimized geometry. The details of geometry optimization and the geometry of different sizes of Ga_mAs_n, Ga_mN_n, and Ga_mP_n molecular clusters studied in this work are reported elsewhere.[15−17] The elements of the polarizability and the first-hyperpolarizability tensors were calculated by using the time-dependent coupled perturbed Hartree−Fock (TDCPHF) method[18] and the same ETG basis set as used for geometry optimization. The exponents of the basis sets are given in related papers.[15−17] The elements of the dynamic polarizability tensor $\alpha(\omega)$ were calculated at two optical wavelengths, $\lambda = 1064$ and 532 nm. The hyperpolarizability tensors $\beta(-\omega;0,\omega)$ corresponding to electrooptic Pockels effect (EOPE) and $\beta(-2\omega;\omega,\omega)$ corresponding to second harmonic generation (SHG) were calculated at $\lambda = 1064$ nm.

III. Results

The clusters used in this study are $GaX_4H_{12}^{3+}$, $XGa_4H_{12}^{3-}$, H_3-$GaXH_3$, $Ga_4X_4H_{18}$, and $Ga_3X_3H_{12}$, where X = N, P, or As. The group III element Ga is common to all the clusters, while the group V elements are represented by N, P, and As. The optimized structures of the Ga_mN_n clusters except for $m = 1$, $n = 1$ are shown in Figures 1−4. Similar structures were obtained

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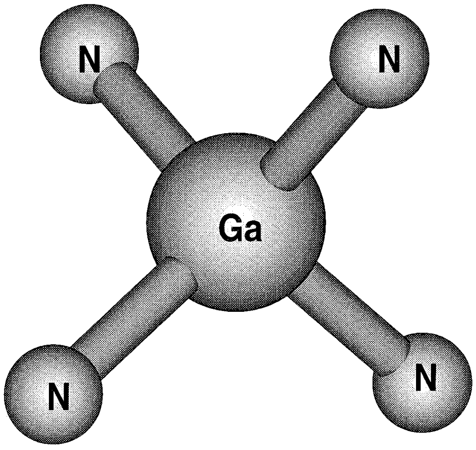

Figure 1. Optimized equilibrium structure of GaN_4 ($q = +3$).

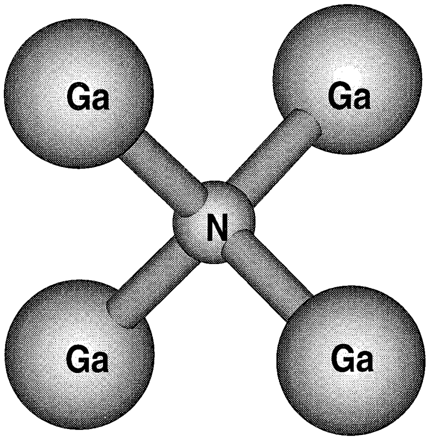

Figure 2. Optimized equilibrium structure of NGa_4 ($q = -3$).

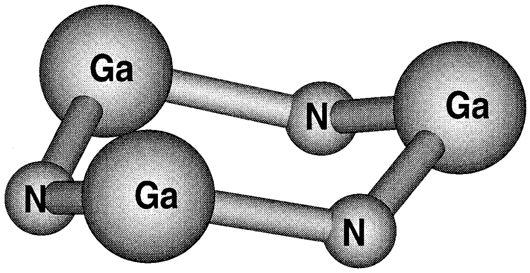

Figure 3. Optimized equilibrium structure of Ga_3N_3.

for the P and As homologues. The optimized geometries are given in related papers.[15−17] The H atoms used as the terminators on the outer atoms are not shown in the figures.

The calculated dipole moments and static polarizability tensors of the GaN, GaP, and GaAs clusters are listed in Tables 1−3. The magnitude of the dipole moment for the same size cluster, as expected, follows the order GaN > GaP > GaAs. The noted order in the dipole moment is consistent with the difference in electronegativities of the group V elements N, P, and As.

Polarizability. The mean polarizability, ⟨α⟩, listed in the tables, is defined as an average of the trace of the polarizability matrix

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (1)$$

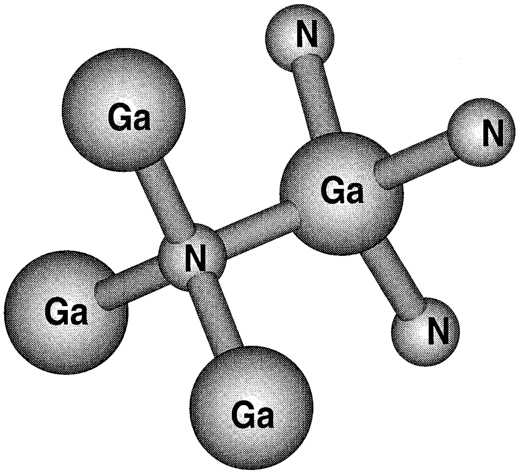

Figure 4. Optimized equilibrium structure of Ga_4N_4.

TABLE 1: Calculated Dipole Moment, μ(D), and Static Polarizability, α(0) (10^{-24} esu^2 cm^2 erg^{-1}), for GaN Clusters

		α			
molecule	μ	*xx*	*yy*	*zz*	⟨α⟩
$GaNH_6$	6.278	4.91	4.91	3.19	4.34
$GaN_4H_{12}^{3+}$	0.000	4.84	4.84	4.84	4.84
$Ga_4NH_{12}^{3-}$	0.000	14.77	14.77	14.77	14.77
$Ga_3N_3H_{12}$	4.348	10.51	10.51	11.46	10.83
$Ga_4N_4H_{18}$	20.118	18.90	14.04	14.04	15.66

TABLE 2: Calculated Dipole Moment, μ(D), and Static Polarizability, α(0) (10^{-24} esu^2 cm^2 erg^{-1}), for GaP Clusters

		α			
molecule	μ	*xx*	*yy*	*zz*	⟨α⟩
$GaPH_6$	5.003	7.02	7.02	7.31	7.11
$GaP_4H_{12}^{3+}$	0.000	16.06	16.06	16.06	16.06
$Ga_4PH_{12}^{3-}$	0.000	21.05	21.05	21.05	21.05
$Ga_3P_3H_{12}$	2.425	23.38	23.38	18.34	21.70
$Ga_4P_4H_{18}$	20.537	31.95	27.89	27.89	29.25

TABLE 3: Calculated Dipole Moment, μ(D), and Static Polarizability, α(0) (10^{-24} esu^2 cm^2 erg^{-1}), for GaAs Clusters

		α			
molecule	μ	*xx*	*yy*	*zz*	⟨α⟩
$GaAsH_6$	4.455	7.51	7.44	7.44	7.46
$GaAs_4H_{12}^{3+}$	0.000	19.51	19.51	19.55	19.53
$Ga_4AsH_{12}^{3-}$	0.005	22.11	22.10	22.10	22.11
$Ga_3As_3H_{12}$	4.779	19.75	19.74	10.17	16.55
$Ga_4As_4H_{18}$	17.892	34.23	30.04	30.04	31.44

For the systems under study the magnitude of the mean polarizability, unlike the dipole moment, appears to depend predominantly on the size of the cluster. The symmetry and the charge state of the cluster appear to have only marginal effects on polarizabilities. It is noted from Table 1 that between $NGaH_6$ and $Ga_4N_4H_{18}$ the polarizability increases by a factor of about 4. A similar trend is noted in the case of P (Table 2) and As (Table 3) clusters. From the calculated results listed in Table 1, the mean polarizability for GaN clusters due to one Ga−N unit is estimated to be approximately 4.0 Å^3. In the case of GaP and GaAs clusters the estimated mean polarizabilities due to one unit of Ga−P and Ga−As are ≈7.3 and ≈7.9 Å^3, respectively.

The mean polarizability value for N-rich clusters is about the same as that for N-deficient clusters having the same number of Ga atoms. This suggests that N atoms do not contribute significantly to the overall polarizability of the Ga_mN_n clusters. Comparison of the mean polarizability for $GaPH_6$ with $GaP_4H_{12}^{3+}$ and $PGa_4H_{12}^{3-}$ (Table 2) shows again that the Ga atom

TABLE 4: Calculated Mean Dynamic Polarizability $\langle\alpha(\omega)\rangle$ (10^{-24} esu^2 cm^2 erg^{-1}) for Ga_nX_n (X = N, P, As) Clusters at Optical Wavelengths $\lambda = 1064$ and 532 nm

	Ga_nN_n		Ga_nP_n		Ga_nAs_n	
n	1064 nm	532 nm	1064 nm	532 nm	1064 nm	532 nm
1	4.37	4.48	7.18	7.39	7.53	7.76
3	10.91	11.16	21.95	22.73	16.74	17.33
4	15.79	16.19	29.60	30.74	31.87	33.27

TABLE 5: Calculated ΔE (HOMO − LUMO) (eV) for Ga_mX_n (X = N, P, As) Clusters

m	n	Ga_mN_n	Ga_mP_n	Ga_mAs_n
1	1	15.10	14.45	14.34
1	4	20.19	14.36	12.73
4	1	15.16	13.30	12.69
3	3	15.50	13.04	13.07
4	4	12.42	10.28	9.34

is a major contributor to the overall polarizability, though the contribution of P atoms appears to be much larger than that of N atoms in an isovalent GaN cluster. In the case of GaAs clusters (Table 3), however, one notices an almost equal contribution by both Ga and As atoms. The reason for this behavior is the fact that Ga and As atoms have higher atomic numbers (Z) than N and P. The valence electrons in high-Z atoms (e.g., As) are more polarizable than those of the low-Z atoms, due to a larger screening by the core electrons in the former.

Between the isoelectronic Ga-rich and As-rich Ga_mAs_n clusters with the same $n + m$, the former have a larger polarizability. A similar trend has been noted in the experiment by Schlecht et al.[11] We also note that the low-temperature experimental result by Schäfer et al.[12] for the Ga_4As_4 cluster per atom for $n + m = 8$ agrees very well with our calculated value of 3.9 Å^3 reported in Table 3. This gives an added confidence in the quality of the results from other systems. A noted difference between the clusters generated by Schlecht et al.[11] and the isoelectronic Ga-rich and As-rich clusters studied in this work is that while the former were perhaps charge neutral, the latter are either negatively charged or positively charged. A direct comparison with experiment using uncharged clusters will be reported in a future communication.

The dynamic polarizabilities, $\alpha(\omega)$, at $\lambda = 1064.0$ and 532.0 nm for the charge neutral clusters are listed in Table 4. One notes from Tables 1−4 that $\alpha(-\omega;\omega)$ increases with the energy (frequency) of the applied field. However, the overall dispersion noted for $\alpha(-\omega,\omega)$ in the range of the frequency of the applied field used in the calculation is small.

A general assumption made in cluster calculations is that with increasing size of the cluster, the energy difference, ΔE, between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases and eventually reaches the band gap ($E_{\mathrm{bg.}}$) limit of the bulk crystalline material. If the bond additivity model[19] is assumed to be valid, as is generally the case in covalent semiconductors, then the polarizability will increase with the size of the cluster, eventually reaching its bulk limit. It is, therefore, useful to examine the evolution of ΔE (HOMO − LUMO) and α with the size of the cluster and find their relationships with other parameters such as the atom type and cluster symmetry. The calculated values of ΔE (HOMO − LUMO) for Ga_mX_n (X = N, P, As) are listed in Table 5. One notes that for Ga_nP_n and Ga_nAs_n, with $n = 1$, 3, 4, the value of ΔE (HOMO − LUMO) systematically decreases. In the case of Ga_nN_n, on the other hand, the value of ΔE (HOMO − LUMO) first increases slightly in going from $n = 1$ to $n = 3$ and then decreases by a large amount.

TABLE 6: Calculated Hyperpolarizability, $\beta(\omega_\sigma;\omega_1,\omega_2)$ (10^{-32} esu^3 cm^3 erg^{-2}), of Charge Neutral Ga_nX_n (X = N, P, As) Clusters[a]

	Ga_nN_n			Ga_nP_n			Ga_nAs_n		
n	static	EOPE	SHG	static	EOPE	SHG	static	EOPE	SHG
1	21.67	22.08	22.94	31.34	32.39	34.64	74.19	76.32	80.87
3	1.23	1.35	1.61	58.41	59.93	63.41	203.87	209.58	221.82
4	229.66	235.27	247.21	383.38	402.72	446.96	278.72	300.35	353.30

[a] β(EOPE) and β(SHG) have been calculated at $\lambda = 1064.0$ nm.

The ΔE (HOMO − LUMO) values for the charged cluster, Ga_mX_n ($m = 1$, $n = 4$; $m = 4$, $n = 1$) are calculated to be larger for the X-rich (X = N, P, As) clusters than for the Ga-rich clusters. Comparing the ΔE (HOMO − LUMO) with α values (Tables 1−3) one notices a certain trend. For example, the decrease in ΔE (HOMO − LUMO) is accompanied by an increase in the value of α. For the same or smaller change in ΔE (HOMO − LUMO) between Ga_nP_n and Ga_nAs_n in going from $n = 1$ to $n = 3$, one notices a larger increase of α in the case of GaP clusters compared to its GaAs homologue. Between $n = 3$ and $n = 4$, the GaAs clusters exhibit a larger change in α than the GaP cluster does. The noted change in α is consistent with the corresponding change in ΔE (HOMO − LUMO).

First hyperpolarizability. Unlike the polarizability, the first hyperpolarizability, β, depends on the symmetry of the atomic cluster. The first hyperpolarizability value for a centrosymmetric system is zero. For systems with nonzero β, one usually observes a vector component, β_μ, directed along the applied electric field. A related quantity, often reported from the theoretical calculations is defined as

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

where β_i ($i = x, y, z$) is given by

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

The clusters in the present study with noncentrosymmetric structures are Ga_nX_n (X = N, P, As), $n = 1$, 3, 4. The calculated first hyperpolarizabilities (β_{vec}) for the static effect ($\hbar\omega = 0$), EOPE, and SHG for these clusters are listed in Table 6. The calculated values listed in the table have been divided by a factor of 2 in order to be consistent with the convention used to represent the experimentally measured values. This difference between the measured β and calculated β arises from the use of different conventions adopted in the experimental and quantum chemical literature.[20]

The calculated values of β exhibit very interesting features. First, the dispersion in β due to various second-order effects at the calculated wavelength ($\lambda = 1064$ nm) is not large. Second, the magnitude of β increases by an order of magnitude when the size of the Ga_nX_n cluster increases from $n = 1$ to 4. Third, the largest increment in β due to cluster size is exhibited by the GaP system. The influence of geometry on the β_{vec} value becomes apparent when one examines the values for the $n = 3$ cluster. Among the various Ga_nX_n clusters used in this study, only $n = 3$ clusters have a ring-type closed structure. This shows that not only the size but also the geometry of the cluster is important for determining the magnitude of hyperpolarizability. The ΔE (HOMO − LUMO) values for GaN and for Ga_3N_3 are almost equal as can be seen from Table 5. However, the first hyperpolarizabilities for the Ga_3N_3 cluster are significantly small. This shows that symmetry has a greater influence than the ΔE

(HOMO − LUMO) on the magnitude of first hyperpolarizability of Ga_nX_n clusters. A comparison of dipole moments for the Ga_3X_3 cluster with those of other Ga_nX_n clusters shows a decrease in the case of GaN and GaP (Tables 1 and 2) and an increase for the GaAs cluster (Table 3). There is a significant increase in the value of the first hyperpolarizability in going from the GaAs cluster to the Ga_3As_3 cluster, while the corresponding increment between the GaP and Ga_3P_3 clusters is quite small. In contrast, in the case of Ga_nN_n, the first hyperpolarizability exhibits a decrease in its magnitude in going from GaN to Ga_3N_3. These results further strengthen the observation that symmetry has a greater role than any other factor, such as the number or type of heteroatoms, or ΔE (HOMO − LUMO), on the first hyperpolarizability of these clusters.

IV. Summary

We have calculated the (hyper)polarizabilities of the tetrahedral Ga_mX_n ($X = N, P, As$) clusters of increasing size and varying charge states. The calculated properties, for the first time, provide new insights into the microscopic structure−(hyper)polarizability relationships in group III−V clusters. First, it is noted that the magnitude of the linear polarizability, α, depends predominantly on the size of the cluster. The Ga atom appears to have a relatively large influence on the polarizability compared to the other atoms. N atoms seem to play only a minor role in the overall polarizability of the Ga_mN_n clusters. Similarly, the charge state of the Ga_mX_n cluster seems to have little influence on the polarizability. The average polarizability per Ga−X ($X = N, P, As$) bond is estimated to be ≈ 4 Å^3 for Ga−N, ≈ 7.3 Å^3 for GaP, and 7.9 Å^3 for GaAs. Our calculated value of $\alpha(0) = 3.9$ Å^3 for Ga_4As_4 is in excellent agreement with the low temperature measured value for the $(n + m) = 8$ cluster reported by Schäfer[12] for GaAs. This lends confidence to our calculated polarizabilities. In all cases the $\alpha(\omega)$ value displays a small but finite dispersion due to the frequency of the optical field.

The first hyperpolarizability, β, for different NLO effects exhibits remarkable dependence on the cluster size and symmetry. The value of β for Ga_mX_n ($X = N, P, As$) increases by an order of magnitude when n increases from 1 to 4. The geometrical features of the clusters appear to have a greater influence than other factors, such as the size and charge state, on the calculated value of β.

It is also interesting to note that the β values for the Ga_4X_4 ($X = N, P, As$) clusters have a magnitude similar to that of the corresponding value calculated for *p*-nitroaniline,[20] a system generally considered one of the most efficient among the second-order active organic molecules. It is therefore possible that suitably engineered Ga_mX_n ($X = N, P, As$) clusters can be of use as efficient photonic systems. The β values show the expected trend of $\beta(\mathrm{SHG}) > \beta(\mathrm{EOPE}) > \beta(\mathrm{static})$. Calculations involving extended clusters and the effects of basis sets on the properties of NLO coefficients are in progress and will be reported in a subsequent communication.

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