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Structures and composition-dependent polarizabilities of open- and closed-shell Ga_nAs_m semiconductor clusters

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A systematic investigation of the structures and the dependence of the dipole polarizabilities on the composition of closed and open shell gallium arsenic clusters is presented. Our investigation focuses on nine gallium arsenide (GaAs) clusters with five and six total number of atoms of systematically varying composition. These clusters are the smallest species of small GaAs clusters which have attracted substantial attention due to their strongly oscillating experimental polarizability values. The ground states of those clusters have been determined using a global approach which combines molecular dynamics and an automatic procedure of comparing and selecting cluster structures based on pattern recognition techniques. The polarizabilities have been studied by means of coupled cluster techniques complemented by a semi-empirical hybrid functional which includes corrections from perturbation theory. Our global structural investigation found two different structures for Ga_4As_2 and Ga_1As_5 which are lower in energy than the previously reported ones. The performed polarizability investigation suggests that open shell GaAs systems composed of five atoms are not more polarizable than closed-shell clusters built by six atoms as is indirectly implied by the reported experimental data. Also, the polarizabilities of those species increase as a function of the number of Ga in a monotonic but not systematic manner. The observed increase type is explained by the large atomic polarizabilities of Ga and in terms of the particular structural and bonding features of a given cluster. Furthermore, the comparison between our theoretical values and earlier experimental polarizability estimations clearly shows that for the five-atomic clusters, the reported experimental polarizability is not largely overestimated as was previously believed. Our results for the six-atomic cluster demonstrate that the polarizability per atom of a six atomic GaAs cluster of any composition is larger than the polarizability of the bulk material, contrary to what has been demonstrated by the experiment.

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I. INTRODUCTION

Apart from the structural, electronic, and spectroscopic properties of metal and semiconductor clusters that have been a subject of a vast amount of studies the recent years [1–4], response properties with respect to an external electric field, such as their polarizabilities [5–13] have also attracted substantial attention. This is not surprising since the electric-dipole polarizabilities of cluster species not only describe the distortion of clusters electronic cloud under the influence of weak external fields but they are also associated with fundamental characteristics of electronic structure such as hardness or softness [14], acidity or basicity [15], the ionization potential [16], the molecular reactivity, or the stability of a given system through the minimum polarizability principle (MPP) [17].

A worth noticing number of previously reported studies [6,18,19] have discussed correlations between various cluster properties (including polarizabilities) and cluster features such as the cluster size, bonding, the shape and the cluster constitution leading to very interesting conclusions. All these kinds of investigations have been motivated by the cornerstone of nanotechnology: *the ability of the nano-objects to alter dramatically their properties as a function of their size and shape due to surface and quantum confinement effects.* In this work we explore two additional cluster features which are expected to play a crucial role in their response to weak external electric fields and in extension to most of their properties. These features are the cluster composition and their electronic structure as the latter depends on the total number of their electron. Our interest is geared toward the way an electronic property such as the static dipole polarizability evolves in the case of open and closed shell nonstoichiometric Ga_nAs_m clusters of different composition extending previous studies which considered mainly stoichiometric species. For this purpose, nine clusters of gallium arsenide (GaAs) of the type Ga_nAs_m, with $n+m=5$ and 6 have been carefully selected. On the one hand the odd-numbered clusters ($n+m=5$) are necessarily systems in which the electrons are not completely assigned to orbitals in pairs (open shell) due to the total number of their electrons. On the other hand, as has been shown earlier [10,23], for the even numbered neutral clusters their closed shell forms, where all electrons are assigned in pairs, comprise the most stable electronic configurations. The specific clusters are the smallest species of a group of a total 12 Ga_nAs_m clusters with $n+m=5$ up to 17 that have attracted intense attention due to their strongly oscillating polarizability values obtained by means of molecular deflection techniques by Schlecht *et al.* [11], Becker *et al.* [13], Schäfer *et al.* [12], and Schnell *et al.* [10] The

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observed behavior has been an area under discussion in several earlier investigations [7–11] and serves as an example of intriguing disagreement between theory and experiment [7,8,24]. This matter attracted our curiosity thus we explored by methods of high predictive capability whether open shell GaAs clusters are significantly more polarizable than the closed shell systems as it has been suggested by the experiment.

Our investigation involves three main parts. The first deals with the determination of the cluster's ground state structures (i.e., the global minima of the potential energy surface) since for some of the clusters we considered, the ground-state structures are unknown. The second part of our investigation, concerns the computation and the study of the properties of interest, while the third one involves the analysis of the evolution of those properties with respect to specific cluster characteristics such as their size and composition. In brief, to determine the ground-states structures of the clusters of interest we relied on molecular dynamics combined with an automatic procedure of comparing and selecting cluster structures based on pattern recognition techniques followed by full geometry optimizations using various methods since as it has been demonstrated the accurate determination of the ground-state structures of clusters it depends not only on chosen computational approach but the method one uses to compute the energy of a given cluster system [20,21]. For the second and third parts of this work, the determination of the dipole polarizabilities and the study of their evolution, we counted on *ab initio* methods of high accuracy. Our computational approach relies on a hierarchy of *ab initio* methods of increasing predictive capability such as the Hartree-Fock (HF) approximation [self-consistent field (SCF)] the Møller-Plesset (MP) many body perturbation theory and also on coupled cluster techniques such as singles and doubles coupled cluster (CCSD), and singles and doubles coupled cluster with an estimate of connected triple excitations via a perturbation treatment [CCSD(T)]. Furthermore, to resolve any computational issues that may rise from the use of a different class of quantum chemical approach we included in our study a newly developed semiempirical hybrid functional which includes corrections from perturbation theory based in the Görling-Levy perturbation theory in which the correlation energy of a given system is calculated considering the Kohn-Sham orbitals. This functional (hereafter B2BLYP) has been recently proposed by Grimme [22] and it is based on a mixing of standard generalized gradient approximations for exchange by Becke and for correlation by Lee, Yang, and Parr with Hartree-Fock exchange and a perturbative second-order correlation part that is obtained from the Kohn-Sham orbitals and eigenvalues.

II. COMPUTATIONAL METHODS

A. Determination of global minima

It is a matter of fact that the determination of the global minimum of an energy potential surface of a cluster is a very difficult task mainly due to the existence of a vast number of local minima even in the case of clusters composed by few atoms [25]. For this reason a respectable number of various global computational schemes have been developed and proposed based on the simulation annealing [26], genetic algorithms [27], the big bang concept [28], and basin hopping techniques [29]. These and other similar methods have been successfully employed to several systems and, as it has been proven, give similar results depending on the level of theory used. One of the main objectives of almost all the developed so called global methods is the determination of all possible physically reasonable configurations of a given cluster that could serve as starting points for further investigation which mainly involves full geometry optimizations and vibrational characterizations.

In this work to resolve the problem of finding in a global manner the suitable configurations which will lead eventually to the ground state structures we used a somewhat different approach. Our scheme is based on a three-step computational strategy which relies on density functional theory (DFT) molecular dynamics, on an automatic selection procedure of cluster structures, and finally, on full geometry optimizations using widely accepted *ab initio* methods and well tested DFT functionals in order to verify the universality of the obtained results. More specifically, in a first step an initial set of structures is obtained by a molecular dynamics (MD) simulation for each cluster using the atom centered density matrix propagation molecular dynamics model (ADMP) procedure as implemented in GAUSSIAN 03[30] package. This simulation is based on the principles of molecular dynamics (based on approximations taken from density functional theory) according to which the atoms of the clusters are allowed to interact for a period of time. This interaction provides a view of their motion. In this work this motion is taken into account as a collection of cluster structures which serves as a set of the physically reasonable relative atom arrangements of the cluster. Each of those structures, which in fact represent snapshots of simulated dynamic motion of the clustered atoms, are compared with all the rest of same initial set of structures with regard to their structural characteristics in the second step of our scheme. This is automatically done using a specified pattern recognition technique which helps us to decide which of the obtained structures could be used as appropriate candidates for a further detailed structural study. Lastly the third and final step of our approach involves full geometry optimizations of the obtained dissimilar clusters structures with a collection of DFT and *ab initio* methods.

Let us now expand in brief each part of the above computational strategy. For the MD simulation the time dependent forces are computed at the Becke's three-parameter exchange DFT functional with the Lee, Yang, and Parr correlation functional (B3LYP) [31] with the Los Alamos National Laboratory (LANL) effective core potential (LANL2) basis set of double ζ quality augmented with one polarization function for each atom in order the hypervalency to be correctly treated. The performed number of particles-volume-temperature (NVT) ensemble simulation has been chosen to last 10 ps with a time step of 0.2 fs. To avoid problems caused by possible large energetic barriers between different cluster configurations the simulation starts from a rather large temperature of 2500 K. In this case though, undesirable cluster dissociations may occur after a few ps. To overcome this difficulty, the simulation has been automatically set to stop each time all interatomic distances (As-As, Ga-Ga, and Ga-As) become larger than two times the atomic distances of the corresponding diatomics As_2, Ga_2, and GaAs. Then, the simulation restarts under a lower temperature which corresponds to 80% of the initial one with a new set of kinetic energies on each atom of the last aggregated structure. The above procedure continues until a set of 50 000 initial cluster structures is obtained.

The pattern recognition scheme considered here is based on concepts of information theory that have been introduced previously by Maroulis [32] in the study of the similarity or dissimilarity of a vast assortment of different computational methods in the calculation of various molecular electric properties (see also Ref. [33]). In the original work of Maroulis the central mathematical object is the theoretical description (or pattern) of molecules as a collection of their electric properties (features) calculated at different levels of theory. For instance, if one computes all the electric properties of a given molecule at the HF level of theory then the collection of those computed values can serve as a unique theoretical description of this molecule at the HF level of theory with respect to its response to an electric field. In the same manner a unique theoretical description of a cluster can be obtained by using as features its interatomic distances. This description can serve as the structural fingerprint of this cluster configuration and it is represented by the following one-dimensional vector:

$$C_i^{TD}\{r_{12}, r_{13}, \ldots, r_{kl}, \ldots, r_{nm}\}, \tag{1}$$

where C_i^{TD} is the theoretical description of each structure i of the initial set of structures and r_{kl} (with $k \neq l$) is the distance between two atoms k and l of the cluster. In this manner each structure that belongs to each initial set of configurations can be represented by a unique vector. In the resulting pattern space one can easily measure the distances D_{ij} between two random vectors C_i^{TD} and C_j^{TD} with $i \neq j$ by defining and applying the appropriate metrics [34] (distance functions). Each distance D_{ij} can work as a criterion that reflects the proximity (or similarity) between two vectors which due to their construction mirror the structural proximity of two different cluster configurations of the same set. For this task we used the very well known Minkowski metric in its Euclidean version ($1/p = 1/2$),

$$D_{ij} = \left(\sum |C_i^{TD} - C_j^{TD}|^p / \max_{i,j} |C_i^{TD} - C_j^{TD}|^p \right)^{1/p}. \tag{2}$$

Large distances (i.e., $D_{ij} \to 1$) should imply configurations characterized by different interatomic distances, thus dissimilar structures, which are expected to lead to different cluster isomers after full geometry optimizations. On the other hand small distances D_{ij} are expected to correspond to cluster isomers of similar structures which most likely would lead to the same stationary points after a full geometry optimization is carried out.

A schematic representation of the above scheme is given in Fig. 1. This figure shows the treatment of Ga_2As_3. In short, after the initial set of 50 000 structures is prepared by an MD simulation and the distances between the theoretical descriptions C_i^{TD} of each structure are obtained, a carefully chosen filter is applied. In this particular case we have chosen all the structures that they are characterized by distances $D_{ij} > 0.27$. As a result of that, we ended up with 33 structures that are the appropriate candidates for a deeper investigation involving reoptimizations at various levels of theory using larger basis sets than the LANL2DZ. This procedure led to seven low lying isomers. Among them the formerly established ground state structure [35] can be easily spotted together with all the previously studied higher lying isomers. The same procedure has been repeated for each cluster of this study.

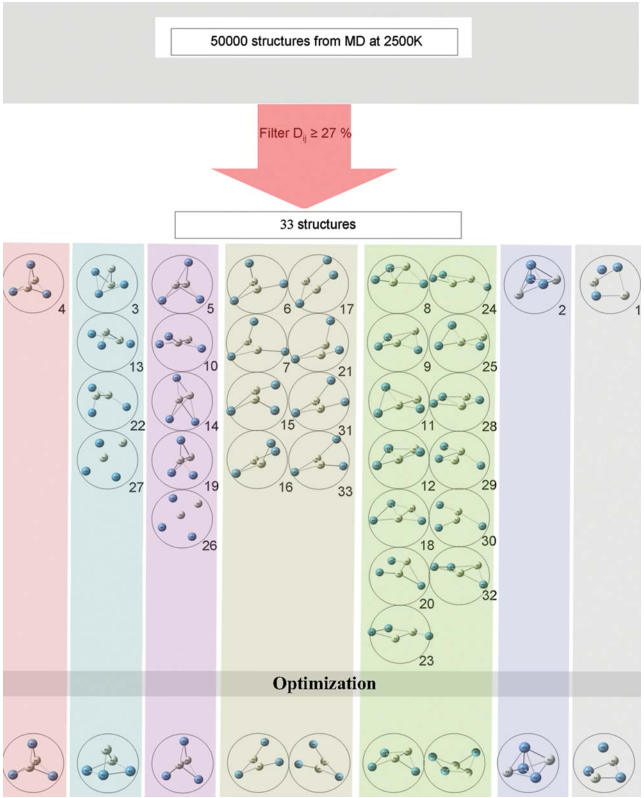

FIG. 1. (Color online) A schematic representation of the employed computational scheme for the determination of the ground-states structures and the low lying isomers of each cluster. This figure presents the treatment of the Ga_2As_3 cluster.

B. Cluster polarizabilities

The perturbed energy of a molecular system in the presence of a weak uniform external static electric field can serve as an efficient information source about the electric response properties [36] such as the polarizabilities and hyperpolarizabilities:

$$E^p = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \ldots . \tag{3}$$

E^p is the energy of the atomic or molecular system in the presence of the static electric field (F), E^0 is its energy in the absence of the field, μ_α corresponds to the permanent dipole moment of the system, $\alpha_{\alpha\beta}$ to the static dipole polarizability tensor and $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$ to the first and second dipole hyperpolarizabilities, respectively. Greek subscripts denote tensor components and can be equal to x, y, and z and each repeated subscript implies summation over x, y, and z.

The dipole moment, the diagonal ($\alpha_{\alpha a}$) and transversal ($\alpha_{\alpha\beta}$) components of the dipole polarizability tensor the mean (or average) static dipole polarizability ($\bar{\alpha}$), the and the anisotropy ($\Delta\alpha$) of the polarizability tensor can be obtained by applying weak electric fields (0.0005–0.001 au) in each α and β directions and $\alpha\beta$ planes of the Cartesian space as follows:

$$\mu_a \approx \frac{E(-F_a) - E(F_a)}{2F_a}, \tag{4}$$

$$\alpha_{aa} \approx \frac{2E(0) - E(-F_a) - E(F_a)}{F_a^2}, \tag{5}$$

$$\alpha_{a\beta} \approx \frac{E(F_a) + E(F_\beta) - E(F_a, F_\beta) - E(0)}{F_a F_\beta}, \tag{6}$$

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \tag{7}$$

$$\Delta\alpha = \left(\frac{1}{2}\right)^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{zy}^2)]^{1/2}. \tag{8}$$

This approach allows one to obtain quite reliable polarizability values [6,7] of a given system using all types of post Hartree-Fock and DFT methods only by computing the energies of the free clusters with and without the field.

For the open shell systems of this study ($n+m=5$) the calculations were carried out using the unrestricted forms of both the *ab initio* and DFT methods we considered. In these forms the wave function is described by two sets of orbitals (one for the alpha and one for the beta electrons). However, it is very well known that unrestricted methods may suffer from errors caused by the so-called spin contamination. The source of the spin contamination is very well known and comes from the fact that the two set wave function is no longer an eingenfunction of the total spin. As results of that, there is always the possibility that some errors may also be introduced to the polarizability values [37]. Spin contamination often is not negligible in unrestricted Hartree-Fock (UHF) and unrestricted Møller-Plesset computations (UMP2 UMP3 UMP4). On the other hand CCSD, CCSD(T) and the approximate DFT functionals do not significantly suffer from those effects (see for instance [38] and refs therein). Thus, for the open shell systems we will present and discuss only the CCSD, CCSD(T), and DFT polarizability results and check, in short, the influence of the spin contamination on the properties of interest using the l-fold spin-projected ($l=1$) PUHF PUMP2 and PUMP3 methods [39].

To finish, since the present case involves a comparative study between systems of different composition, basis sets of the same type have been used in order to obtain reliable estimations of the relative property magnitudes over all the cluster compositions. For all clusters we used the all electron augmented correlation consistent polarized valence double zeta basis set [40] aug-cc-pVDZ of the small core pseudopotential (PP) or electron core potential type.

III. RESULTS AND DISCUSSION

A. Structural data

Figure 2 illustrates the predicted ground state structures and selected low lying isomers of each GaAs cluster considered in this work optimized using the one parameter 1996 exchange functionals of Perdew, Burke, and Ernzerhof combined with the correlation functional of the same authors [41] (PBE1PBE, hereafter PBE0). All the clusters included in this figure correspond to true minima characterized by all real vibrational harmonic frequencies. In the case of the odd-numbered clusters the predicted global minima for Ga_1As_4, ($^2A_1$-C_{2v} electronic state), Ga_2As_3 ($^2A_2''$-D_{3h}), Ga_3As_2 ($^2A_1$-C_{2v}), and Ga_1As_4 ($^2A_1$-C_{2v}) correspond to the same clusters that have been established in the literature as the ground-state structures [35,42,43]. Concerning the ground-state structures of Ga_3As_3 ($^1A'$-C_s), Ga_2As_4 ($^1A_{1g}$-C_s), our results are consistent with earlier investigations [44] (see also Ref. [45] and references therein). For Ga_4As_2 our computational scheme led to a global minimum which is different than those reported before by Lou *et al.* [42] within the local spin density (LSD) approximation and by Feng *et al.* [44] based on the Becke's three parameter hybrid functional using the correlation functional of Lee, Yang, and Parr (B3LYP). Instead of the C_{2v} edge capped trigonal bipyramidal shape that was proposed by Lu *et al.* and its corresponding face capped bipyramidal shape (^1A) in the C_1 symmetry point group found by Feng *et al.*, two other totally different configurations, one on C_{2v} ($^1A_1$) and one in C_2 (^1A) symmetry are lower in energy. This outcome has been verified by geometry optimizations performed at MP2, B3LYP, and levels of theory using basis set of different type and construction such as 6-31G(2d) and cc-pVDZ. The two new configurations are extremely close in energy and they are expected to compete for the ground state structure. For instance, geometry optimizations performed at the PBE0 level with the 6-31G(2d) basis set at the level yield the C_{2v} isomer as lower in energy by 0.09 eV (1.93 kcal). In striking contrast MP2 geometry optimizations with the 6-31G(2d) set of Gaussian basis functions, favor the C_2 isomer by 0.05 eV (1.18 kcal). What is more, MP2 single point computations with the 6-311G(3d2f) basis set taking all electrons into account (Full MP2) and PBE0 calculations at the MP2 optimized geometries, yield the C_2 configuration lower in energy while PBE0 and MP2 computations using the 6-311G(3d2f) basis set on the PBE0 optimized geometries return the opposite ordering. Obviously, we are dealing with a special case of cluster for which the potential energy surface (PES) global minimum greatly depends on the geometry optimization method. For this reason, we considered both of those isomers

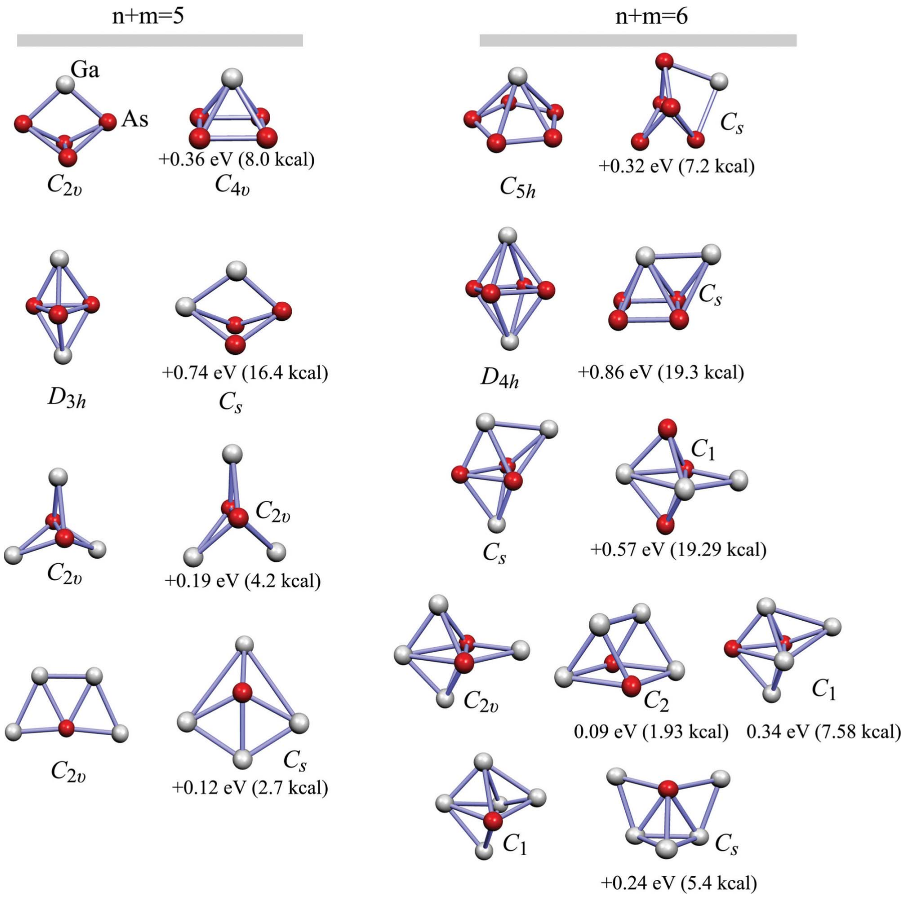

FIG. 2. (Color online). Ground-state structures and selected low lying isomers along with the respective energy separations (kcal) of each of each Ga_nAs_m cluster with $n+m=5$ and 6. All equilibrium geometries were optimized at the PBE0 level using the 6-31G($2d$) basis set.

in our polarizability study. Lastly, for Ga_1As_5 our approach suggests that a pentagonal pyramidal configuration ($^1A_1$-C_{5v}) is the global minimum of the last As-rich cluster of the series which is lower in energy than the tetragonal prism proposed by Feng *et al.*

The binding energies of both cluster families are schematically given in Fig. 3(a) as a function of the number of the Ga atoms in each cluster's framework. In this graph we have inserted as well the binding energies of the ground state structures of As_5 [46], As_6 [46], Ga_5 [47], and Ga_6 [47] at the same level of theory. It is more than evident that the electronic stability of the clusters increases with the size of the cluster while decreases with the number of Ga atoms.

At this point it would be very interesting to discuss the relative stabilities among the six-atom clusters of different compositions and compare them with previous mass spectrum measurements in clusters generated by laser evaporation of a pure GaAs disk by O' Brien *et al.* [4]. As it has been reported in this pioneering experimental study, Ga_3As_3 is the dominant species in the six-atom region. Also, in the same work it is reported that 70% of the generated six-atom clusters were Ga_3As_3, 20% Ga_4As_2, and only 10% were Ga_2As_4. Interestingly, the measured composition distribution was found considerably concentrated in Ga_3As_3 contrary to what would be expected by assuming that the clusters formation was a random issue due the occurring atoms collision. As a result of that in the case of the six-atom clusters O' Brien *et al.* observed a deviation from the respective distribution in clusters of larger sizes which closely followed a binomial curve. According to their arguments this should be caused by unknown details in binding energies and the reaction dynamics during the collision based cluster formation process. However, as it clearly seen in Fig. 3 the evolution of the ground state structures binding energies of the six-atom clusters decreases with the number of the Ga atoms. This could only imply that during the experimental process the observed distribution should not be an issue the cluster binding energies. This indirect conclusion is also supported by the second difference in energy (or disproportionation energy): $\Delta_2E_n(n)=E_{n+1}-2E_n+E_{n+1}$ where E_n is the total electronic energy of the clusters with n Ga atoms. This quantity can be used as a stability measure for clusters with n Ga atoms in comparison with clusters composed by $n+1$ and $n-1$ Ga atoms, and it has been routinely used for the identification of "magic" clusters characterized by exceptionally high stability. The obtained results at PBE0, MP2 levels of theory with the 6-31G($2d$) basis set computed on the equilibrium geometries are shown in Fig. 3(b). As it is clearly seen, the disproportionation energy $\Delta_2E_n(n)$ is positive for all the three Ga_2As_4, Ga_3As_3, and Ga_4As_2 clusters and this verifies their stability. On the other hand, the relative stabilities of the three clusters which are the most abundant in the experiment decrease at both levels of theory. For instance, Ga_2As_4 is more stable than its two nearest neighbors Ga_1As_5 and

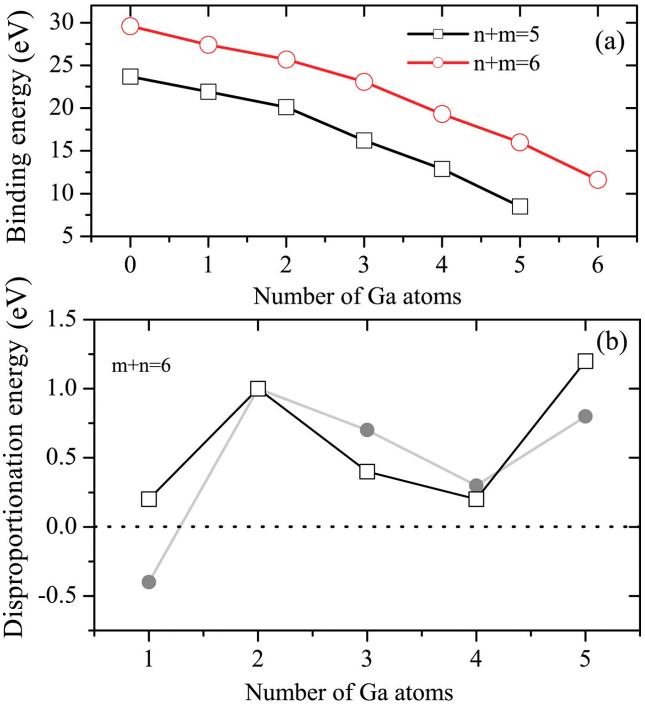

FIG. 3. (Color online) (a) Ga_nAs_m binding energies of at PBE0 level with the 6-31G(2*d*) basis set. (b) disproportionation energy computed with the PBE0 (open squares) and MP2 (filled circles) methods.

Ga_3As_3 while as it might be expected Ga_1As_5 is more stable than Ga_5. In any case though, the revealed trend in the computed binding energies is not linked with the measured composition distribution reported by O'Brien *et al.* Hence, it is still hard to understand or explain the measured composition distribution of the six-atom species and the unexpected high abundance of the stoichiometric species in terms of their binding energies and their relative energetic stability. Most likely the answer hides on the reaction dynamics during the cluster formation and the large number of stable isomers that can be formed by the combination of three Ga and three As, as it has been shown by Balasubramanian [25] using purely mathematical enumeration rules. Also a detailed study of the dissociation energies and the fragmentation paths would be useful in order to resolve this problem which however is beyond the scope of this study.

B. Cluster polarizabilities: Methodological issues

Table I summarizes the computed polarizabilities and polarizability anisotropies of the Ga_nAs_m ground state structures with $n+m=6$. As it shown in Fig. 4 for the closed shell systems the electron correlation contributions to the mean polarizabilities follow a specific pattern. For the clusters with $n \geq m$ the inclusion of electron correlation contributes positively, while the opposite is observed for those with $n < m$. Interestingly, for the clusters with larger number of Ga atoms the observed methods behavior resemble the one observed for Ga_6. On the other hand, for the species with larger or equal number of As atoms the method performance resembles that of As_6.

TABLE I. Mean polarizabilities and polarizability anisotropies of the Ga_nAs_m clusters with $n+m=6$ at RHF, MP2, MP4, CCSD, CCSD(T) and B2PLYP levels of theory with the aug-cc-pVDZ basis set.

	$\bar{\alpha}$ $/e^2\alpha_0^2E_h^{-1}$	$\Delta\alpha$ $/e^2\alpha_0^2E_h^{-1}$
Ga_1As_5-C_{5v}		
HF	186.73	35.30
MP2	191.31	43.31
MP4	191.59	44.05
CCSD	188.23	40.97
CCSD(T)	189.69	42.22
B2BLYP	188.91	44.74
Ga_2As_4-D_{4h}		
HF	194.83	64.65
MP2	197.26	69.38
MP4	197.54	68.09
CCSD	194.57	65.50
CCSD(T)	195.71	66.96
B2BLYP	193.75	63.30
Ga_3As_3-C_s		
HF	211.42	106.71
MP2	219.92	121.45
MP4	218.77	121.15
CCSD	213.31	114.39
CCSD(T)	215.41	117.17
B2PLYP	213.25	115.88
Ga_4As_2-C_{2v}		
HF	229.89	102.04
MP2	233.53	115.41
MP4	230.30	112.94
CCSD	227.01	106.19
CCSD(T)	228.24	108.89
B2PLYP	225.24	117.90
Ga_4As_2-C_2		
HF	230.54	124.49
MP2	233.12	122.27
MP4	228.90	117.37
CCSD	226.46	117.51
CCSD(T)	227.10	117.31
B2PLYP	224.10	114.85
Ga_5As_1-C_s		
HF	237.04	56.14
MP2	230.62	42.07
MP4	226.43	42.16
CCSD	227.83	46.97
CCSD(T)	227.17	45.41
B2PLYP	224.01	43.74

As discussed in a previous section, for the odd-numbered clusters of this study we only present the CC and DFT values which are not expected to carry significant errors due to spin

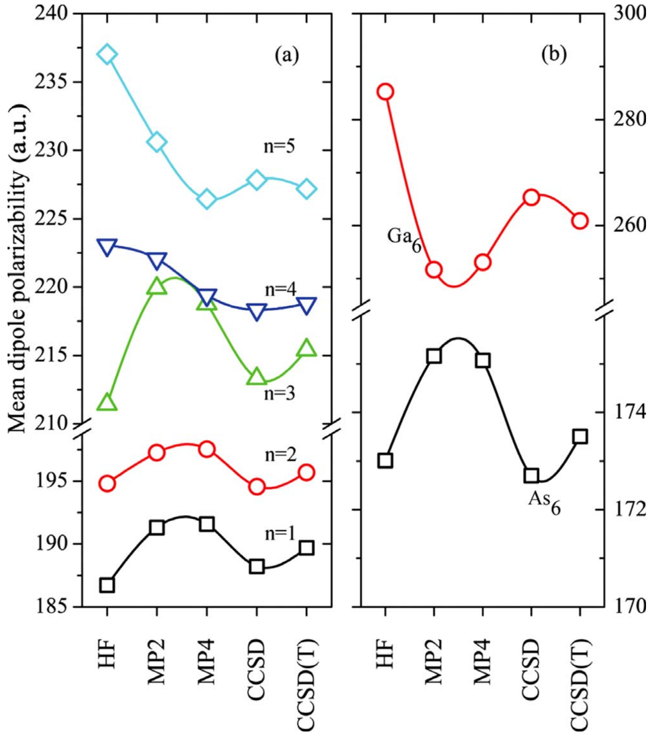

FIG. 4. (Color online) (a) Method performance on the computation of the mean polarizabilities of Ga_nAs_m clusters with $m+n=6$. (b) Method performance on the computation of the mean polarizabilities of Ga_6 and As_6 clusters.

TABLE II. Mean polarizabilities and polarizability anisotropies of the Ga_nAs_m clusters with $n+m=5$ at CCSD, CCSD(T), and B2PLYP levels of theory with the aug-cc-pVDZ basis set.

	$\bar{\alpha}$ $/e^2\alpha_0^2E_h^{-1}$	$\Delta\alpha$ $/e^2\alpha_0^2E_h^{-1}$
Ga_1As_4-C_{2v} $(^2A_1)$		
UCCSD	156.85	34.87
UCCSD(T)	157.86	35.45
UB2PLYP	157.51	36.34
Ga_2As_3-D_{3h} $(^2A_2'')$		
UCCSD	169.79	90.12
UCCSD(T)	168.68	85.97
UB2PLYP	166.62	82.93
Ga_3As_2-C_{2v} $(^2A_1)$		
UCCSD	192.82	57.64
UCCSD(T)	195.67	61.62
UB2PLYP	194.08	61.91
Ga_4As_1-C_{2v} $(^2A_1)$		
UCCSD	219.80	162.89
UCCSD(T)	221.72	165.79
UB2PLYP	219.47	166.30

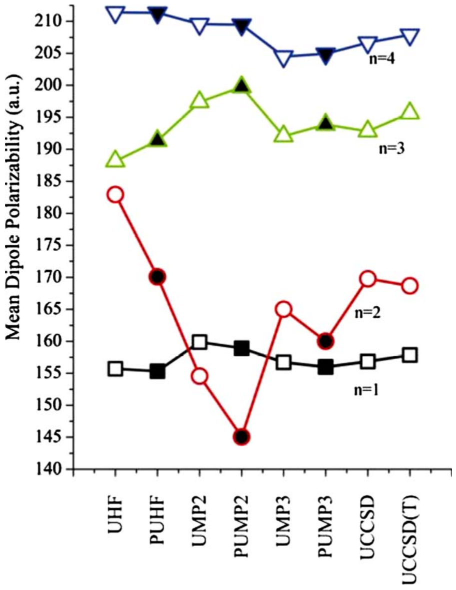

FIG. 5. (Color online) Method performance in the case Ga_nAs_m clusters with $n+m=5$.

contamination. These values are listed in Table II. We also checked the importance of the spin contamination on the computed mean polarizabilities at the rest levels of theory used in this work by using the spin-projected PUHF, PUMP2, and PUMP3 methods. A comparison among the predicted polarizabilities obtained by these methods and the corresponding UHF, UMP2, UMP3, CCSD, CCSD(T) values is schematically presented in Fig. 5. For Ga_1As_4, Ga_3As_2, and Ga_4As_1 a rather smooth variation of the mean values of $\bar{\alpha}$ is observed. In striking contrast, the method performance in the case of the ground state of Ga_2As_3 is entirely dissimilar. First, both the projected and unprojected second-order MP methods yield large electron correlation corrections on the mean polarizability values with respect to the uncorrelated UHF and PUHF. The large mean polarizability differences are caused by the difficulty of the MP series to describe the polarizability component along the C3 cluster symmetry axis. More specifically, the corresponding values at the MP2, MP3, and MP4 levels of theory are of 185.61, 217.18, 194.98 a.u. respectively, while the most accurate level of theory of this work namely the CCSD(T) level, the obtained value of the polarizability component along the C3 axis is of 225.99 a.u. On the other hand the obtained values for the perpendicular components on the C3 axis are remarkably stable: 139.06 a.u. at MP2 level, 138.90 a.u. at MP3, and 139.89 at MP4. All these values are in very good agreement with the one obtained at the CCSD(T) level of theory which is of 140.00 a.u. Second, the differences between the projected and unprojected values both at HF and MP2 levels are larger than it is observed for the other clusters. This indicates strong spin contamination. Nevertheless, as the amount of electron correlation increases, going from the second-order MP to the third, the respective methods divergence between the projected and unprotected versions lessens and the method performance taking into account the PUHF, PUMP3, and CC values resembles the analogous of the rest open shell clusters. Accordingly, the MP values converge to those obtained with the reference CCSD and CCSD(T) in accordance to a very recent study in the case of selected organic molecules [48].

Finally, it is important to stress that among the less computationally expensive correlated methods of this study,

TABLE III. Comparison between the mean polarizabilities and polarizability anisotropies obtained with various *ab initio* and DFT methods for Ga_1As_4 and Ga_2As_3.

Method	$\bar{\alpha}$ $/e^2a_0^2E_h^{-1}$	$\Delta\alpha$ $/e^2a_0^2E_h^{-1}$
Ga_1As_4-C_{2v}		
UCCSD(T)	157.86	35.45
UCCSD	156.85	34.87
UB2PLYP	157.51	36.34
UMP2	159.87	36.37
UB3LYP	156.90	52.38
UMPWPW91	157.62	53.65
UPBE0	155.44	50.78
Ga_2As_3-D_{3h}		
UCCSD(T)	168.68	85.97
UCCSD	169.79	90.12
UB2PLYP	166.62	82.93
UMP2	154.58	46.55
UB3LYP	165.22	114.25
UMPWPW91	165.08	114.51
UPBE0	165.65	118.93

namely the MP2 and B2PLYP approximations, our values show that the latter yields polarizability values close to those obtained at the CCSD(T) level. What is more, from the values given in Table III it is maid clear that B2PLYP with the aug-cc-pVDZ basis set provides a very good description, with respect to the CCSD(T) results, both for the polarizabilities and polarizability anisotropies of Ga_1As_4, Ga_2As_3, and Ga_3As_2 compared to other widely used DFT functionals and in some cases even better than those obtained at MP2 level. The good predictive capability of this method in this class of molecular properties has been also highlighted recently by Christodouleas *et al.* [49].

C. Polarizability evolution

Figure 6 shows the mean polarizability evolution as a function of the number of Ga atoms for each cluster ground state at CCSD, CCSD(T), and B2PLYP levels of theory. In this graph we have also inserted the polarizabilities of the ground-state structures of As_n and Ga_n with $n=5$ and 6 along with the evolution of the respective sum of atomic polarizabilities [50–53] for each cluster constitution in order to make the obvious comparisons.

As it is clearly seen in Fig. 6, for both cluster sizes the binary systems are more polarizable, (more sensitive to external electric fields), than the monoatomic arsenic ones and less polarizable (less sensitive to external electric fields) than the corresponding pure Ga clusters. The clusters mean polarizabilities increase gradually with respect to the number of gallium atoms approaching the computed polarizability values of Ga_6 and Ga_5.

The observed type of polarizability evolution versus the number of Ga atoms in a cluster's framework can be explained in terms of the atomic polarizabilities of Ga and As atoms. Indeed, the polarizability of the Ga atom is almost twice [50] the polarizability of As, thus each time an As atom is replaced by Ga the polarizability of the system increases. On the other hand, as it is seen in Fig. 7 which illustrates the polarizabilities of the three lowest lying isomers of Ga_2As_4, Ga_3As_3, and Ga_4As_2 clusters the rather random increase pattern of those values is caused by the structural and bonding characteristics of each cluster.

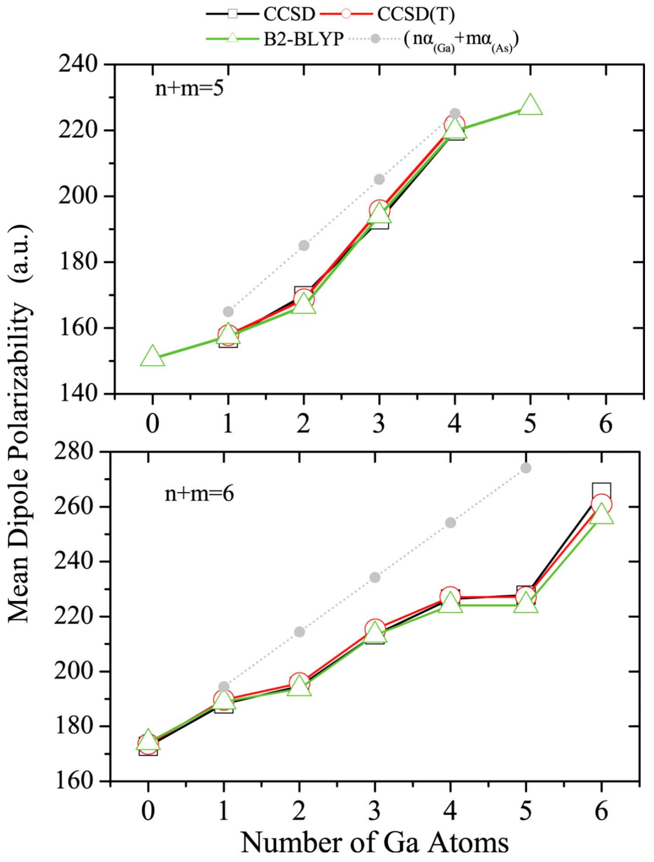

FIG. 6. (Color online) Evolution of the computed mean polarizabilities of the open and closed shell GaAs clusters as a function of the number of Ga atoms, in comparison with the sum of the atomic polarizabilities for each cluster $(n\bar{a}_{Ga}+m\bar{a}_{As})$.

Lastly, it is worth noticing that for all clusters regardless the composition or electronic structure the polarizabilities of the lowest energy configurations are smaller than the sum of the atomic polarizabilities of their constituent atoms. This is in accord with the minimum *polarizability principle* [54] according to which "the natural direction of evolution of any system is toward a state of minimum polarizability." As the size of the cluster rises from $n+m=5$ to 6 the observed deviations between the predicted polarizabilities and the sum of the atomic polarizabilities for each cluster increase, with the number of the Ga atoms. Interestingly, the polarizability increase corresponds to the reverse evolution of the binding energies of each cluster (see Fig. 1) demonstrating that as the polarizability increases the electronic stability of the clusters decreases as this reflects on their binding energies.

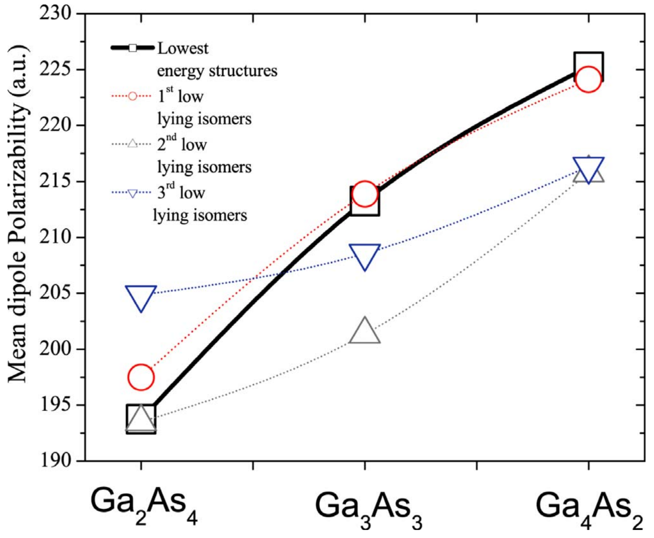

FIG. 7. (Color online) Comparison among the polarizabilities of the ground states and three of the low lying isomers of Ga_2As_4, Ga_3As_3, and Ga_4As_2. All values are computed at the B2PLYP level with the aug-cc-pVDZ-PP basis set.

D. Comparison with the experiment

As we mentioned, the clusters considered here are the smallest GaAs species for which experimental polarizability values from direct measurements are available. However, the previous attempts to compare those values with polarizabilities predicted by various theoretical methods have been proven rather unsuccessful. For instance, in their work Vasiliev *et al.* [8] reported values for Ga_2As_3 ($\bar{\alpha}/\text{atom} \equiv 32.32$, $\bar{\alpha} \equiv 161.6\ e^2\alpha_0^2E_h^{-1}$) and Ga_3As_2 ($\bar{\alpha}/\text{atom} \equiv 34.89$, $\bar{\alpha} \equiv 174.4\ e^2\alpha_0^2E_h^{-1}$) which are significantly smaller than the experimental estimations since for this cluster a value of 185 [55] $e^2\alpha_0^2E_h^{-1}$ has been reported. Even in the case in which one assumes that the measured quantity in the experiment reflects an average value of the polarizabilities of both Ga_2As_3 and Ga_3As_2 the predicted theoretical value is about 17 $e^2\alpha_0^2E_h^{-1}$ below the experimental value. On the other hand, the experimental polarizability of the six atomic of 160 $e^2\alpha_0^2E_h^{-1}$ is significantly smaller than the theoretical predictions for Ga_3As_3 (which is the dominant configuration in the experiment) according to two recent studies [7,45]. Furthermore, there is also one more puzzling issue that emerges from the reported experimental values and have never been discussed before; the six-atomic cluster appears, surprisingly, less polarizable than the one composed by five atoms. As a results of that the polarizability per atom ($\bar{\alpha}/\text{atom}$) of 26.7 $e^2\alpha_0^2E_h^{-1}$ of the six-atomic cluster) appears below the Clausius-Mossotti bulk value ($\alpha_{Bulk} \equiv 28.9\ e^2\alpha_0^2E_h^{-1}$) [10]. Again, both of the above described issues have neither been verified by earlier computations on closed and open shell species up to eight atoms within the DFT framework by Vasiliev *et al.* [8], nor by recent *ab initio* calculation on closed shell systems up to 18 atoms by two of the authors of this study [7,45] which clearly pointed out that stoichiometric GaAs clusters are characterized by larger polarizabilities per atom than the bulk.

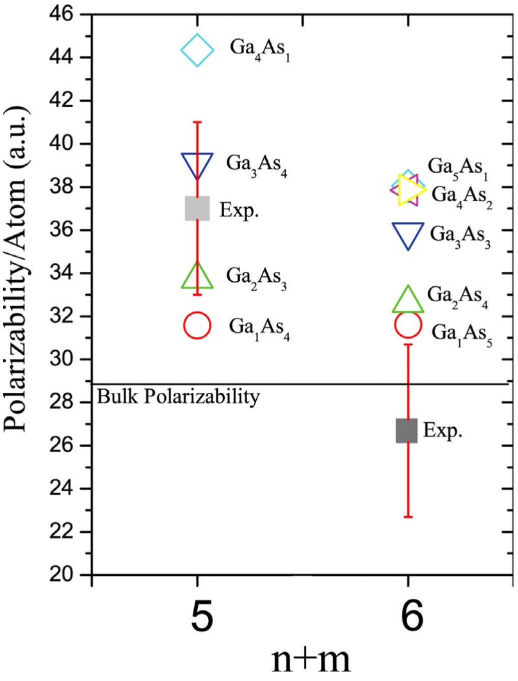

FIG. 8. (Color online) Comparison among the experimental polarizabilities of Ga_nAs_m ($n+m=5,6$) taken from Ref. [10] and the theoretical predicted ones at the CCSD(T) level of theory with the aug-cc-pVDZ basis set.

It is evident that all the previous issues make an interesting puzzle and it is not surprising that several attempts have been maid in order a reasonable explanation to be given. Accordingly, all the previous reports tried to rationalize the possible reasons for which the polarizabilities of an open shell system appears significantly enhanced in comparison with the polarizability of a closed shell clusters of similar size. At first this effect had been attributed to the open shell electronic structures itself and the existence of donor and acceptor like electronic states [12,13]. This interpretation have been partially revised after an in-depth theoretical analysis of the experimental results by Schnell *et al.* [10] which pointed out that "a slight reversible-adiabatic alignment of the clusters dipole moment in the electric field increases the average beam deflection and, eventually the delivered experimental polarizability values." This means that clusters which carry a dipole moment are expected to artificially appear more polarizable in the specific experiment than clusters which are characterized by zero or very small dipole moment values.

Let us now see how our values can fit on the already obtained picture by the most recent reported experimental polarizability values [56] since for both cluster sizes we considered all the possible cluster compositions which may also influence the delivered experimental polarizability while for the five-atomic ones we studied the true ground state structures [57]. Figure 8 visualizes the aforementioned comparison using the values obtained from this study. It is more than evident that the experimental polarizability of the five-atomic cluster is not larger than both the theoretical predicted ones for Ga_2As_3 and Ga_3As_2 as it was believed. Instead, it resides between these two computed values which yield an average of 180.5 $e^2\alpha_0^2E_h^{-1}$ that is only 4.5 $e^2\alpha_0^2E_h^{-1}$ below the experimental one. Interestingly, if one makes the rational assumption that the measured polarizabilities contain contributions from other cluster compositions such as $GaAs_4$ and Ga_4As then their average raises up to 185 $e^2\alpha_0^2E_h^{-1}$ and matches with the experimental one. Of course, this sort of agreement is not strong enough for one to claim that the *ab initio* results of this work reproduce the experimental value of this cluster. This is because first, there is not a clear picture about the relative composition of each cluster in the experiment; second, there is no guaranty that the ground-state structures we found in this work are the ones that are being measured during the experiment; third, temperature effects are not taken into account. Nonetheless, our results give strong evidences that at least for this cluster the experimental polarizability most likely is not largely overestimated due to the effects that are well described by Schnell *et al.* [10].

The above picture is also supported by the obtained values of the clusters dipole moments. More specifically, in the work of Schnell *et al.* the estimated dipole moments for all clusters up to 17 atoms are smaller than 1.0 D, while, the average dipole moments for clusters with five atoms is expected to be less than 0.3 D. Our CCSD(T) results suggest that in the case in which one assumes that during the experimental determination of the dipole polarizability, clusters of all compositions coexist in the measured species, then the derived average theoretical dipole moment is 0.23 D at the CCSD(T) and 0.20 D at the PBE0 level of theory. Both values are found close to the range predicted by the experiment at 12 K (0.21 D) and less than the limiting values of 0.3 D. This observation is rather enlightening since previous theoretical computations [10] predicted an average dipole moment of 0.47 D for Ga_2As_3 and Ga_3As_2 that has been found too large to explain the experimental observations according to the analysis by Schnell *et al.*

So far the obtained theoretical polarizability predictions seem to be reasonable compared to those that are extracted by the previous experiments. The better agreement is owed to the consideration of the true ground-state structures and on values calculated at more accurate levels of theory. Nonetheless, the situation in the case of the six-atomic closed shell systems is different. All the polarizabilities of the ground state structures are found between 189 and 227 $e^2\alpha_0^2E_h^{-1}$. Their total average value is of 213 $e^2\alpha_0^2E_h^{-1}$ resides about 53 $e^2\alpha_0^2E_h^{-1}$ above the experimental value. Even in the case one assumes that the measured species contain only the most dominant composition which is the stoichiometric one built up by three atoms of each kind still the predicted polarizability is too large compared to the experimental one. Interestingly, the pure As_6 cluster is also found about 10 a.u. above the bulk polarizability [57] of GaAs thus the fact that the polarizabilities of mixed GaAs, cluster with six atoms are larger than the bulk polarizability [57] of GaAs should not surprise us. Hence, considering that in all the previous experiments studies the most dominant composition is the stoichiometric one built up by three atoms of each kind, it is rather difficult to find, or even draw a reasonable cluster structure composed by Ga and As which would be characterized by so small polarizability such the one found in the experiment. This can leave us only two options in interpreting the results: either the experimental predicted polarizability for this cluster should be for some reason significantly underestimated, or the real structures of the measured clusters are characterized by dramatically more compact structures than the ones predicted by theoretical geometry optimizations since the more compact the structure is the less polarizable it becomes.

IV. SUMMARY

In this work we have carried out a systematic investigation of the structures and polarizabilities of selected GaAs clusters. First, our structural investigation yielded to two new structures for Ga_4As_2 and Ga_1As_5 which are lower in energy than the previously reported as ground states. Second, our property investigation based on *ab initio* methods of high predictive capability suggests that for small sizes the Ga-rich clusters are expected to be more sensitive to an external electric field than As-rich cluster species. This can be explained in terms of the atomic polarizabilities and of the particular structural features of a given cluster. The latter plays an important role in the amount of the polarizability differences between the various species composed by the same number of atoms. Third, our results clearly point out that the open shell GaAs systems composed by five atoms are not significantly more polarizable than closed shell clusters built by six atoms as it can be understood by the reported experimental values. Also, for the five-atomic clusters it is suggested that the experimental polarizability most likely is not largely overestimated as it was previously believed due to the clusters dipole moment. Furthermore, a more rational interpretation of the experimental results could be obtained by taking into consideration other cluster compositions than Ga_3As_2 and Ga_2As_3. In striking contrast, for the six-atomic clusters a rather different picture emerges since our theoretical results suggest that if there is a minimum polarizability value per atom of a cluster composed by n Ga atoms and m As with $m+n=6$ this value should be larger than the bulk GaAs polarizability per atom and larger than the reported experiment polarizability of the cluster of this size. Finally from the methodological point of view the excellent performance of the B2PLYP functional in the prediction of the polarizabilities of small clusters has to be highlighted.

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[56] In this section by taking into account the most recent experimental study reported by Schnell *et al.* (Ref. [10]) in fact we revisit all three previously reported experimental studies (Refs. [11–13]) since for those two clusters all the reported experimental attempts delivered more or less similar values.

[57] Vasiliev *et al.* considered another structure as the ground state which in this study is found to be the second lowest. Also the majority of the clusters grounds states carry dipole moments which are very large to be consistent with the experimental observations which suggested that the dipoles moments of the clusters with six atoms are negligible. Even for Ga_2As_4 which is characterized by vanishing dipole moment due to its symmetry the computed polarizability is more than 30 $e^2a_0^2E_h^{-1}$ above the experimental one.