Theoretical study of Ga-doped magnesium mineral based on the atomic cluster level: gas-phase GaMgn- (n=2-12) DFT investigation

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Abstract

The geometrical structure, electronic structure and chemical bond properties of the gas-phase GaMg \(n\) - (\(n=2-12\)) clusters were studied utilizing CALYPSO software as well as density functional theory (DFT). It is shown that tetrahedral-like and pyramidal-like structures are the two "seeds" for GaMg \(n\) - (\(n=2-12\)) clusters growth. Relative stability calculations indicate that GaMg 8 - cluster possesses the most robust stability and is a reasonable candidate for the "magic" cluster. NCP calculations confirm that Ga and Mg atoms play the roles of receiving and losing electrons, respectively. NEC analysis further yields that valence orbital electron transfer is \(s \rightarrow p\). ELF analysis shows that Mg-Mg covalent bonds start to appear in GaMg 2 - size, which is much earlier than in other "heavy" metal-doped magnesium. For the most stable GaMg 8 - cluster, UV-Vis, IR and Raman spectroscopic predictions were also performed specifically, and the excited state properties of this cluster were investigated by the hole-electron method and NTO.

1. Introduction

Magnesium, as the lightest structural metal among alkaline earth metals and an essential mineral for the human body, is widely used as materials for the aerospace industry and optical instruments [1, 2], as well as research on the role of magnesium ions in clinical medicine, nutrition and physiology [3, 4]. It is well known that the crystal structure of pure magnesium mineral possesses hexagonal close-packed (hcp) lattice, and such structure determines the low plasticity of pure magnesium crystal [5]. However, hcp structure makes it possible for different magnesium-based alloys to exhibit interesting mechanical properties, which continues to attract researchers' interest. Macroscopically, for example, magnesium-based alloys doped with rare earth metals (Gd, Y, etc.) are proved to have higher strength than ordinary magnesium-based alloys [6]. Microscopically, the nature of the electrons and structure of magnesium crystals with hcp structure can be studied by calculations based on the quantum chemical level, such as the first principle [7, 8] and density functional theory (DFT) [9]. These studies on magnesium and magnesium-based crystals are based on the fundamental principle that the structure of a system determines all physical and chemical properties. Thus, regardless of the scale and theoretical level, the properties of magnesium-based minerals will change whenever their structure differs, and therefore, at least theoretically, are worth investigating. Interestingly, the science of atoms and molecular clusters provides many possible stable structures for magnesium-based substances that do not exist in the bulk state [10].

The motivation of this work is to study the magnesium-based system at the atomic cluster level, which implies the formation of a relatively stable structure when magnesium and dopant atoms are aggregated based on the quantum mechanical physical background. The study of magnesium-based clusters has already yielded some interesting results. For example, Xi et al. [11] and Li et al. [12] studied Sr- and Sr\(_2\)\(^{-}\) doped Mg\(_n\) (\(n = 2-12\)) atoms based on DFT and found that SrMg\(_9\) and Sr\(_2\)Mg\(_8\) have a tower-like structure and higher stability than others. Zhu et al. found that AuMg\(_9\) cluster with a kind of double vertex tent structure shows the strongest stability in all AuMg\(_n\) (\(n = 2-12\)) clusters [13]. Zeng et al. investigated
BeMg\(_n\) (n = 2–12) clusters using a similar approach and also obtained that BeMg\(_9\) cluster has a similar structure and high stability [14, 15]. Zhao et al. [16] and Zhang et al. [17] further researched medium-sized beryllium doped magnesium clusters and found BeMg\(_{16}\) and Be\(_2\)Mg\(_{15}\) clusters present a “spherocone-like” structure as Mg\(_{17}\) cluster studied by Xia et al. [18]. The structures and electronic properties of SiMg\(_n\), PdMg\(_n\), CMg\(_n\), GeMg\(_n\) and SnMg\(_n\) (n = 2–12) clusters were fully investigated by Zhu et al. [19, 20] and Zeng et al. [21] using DFT. Interestingly, they concluded that Si-, Pd-, C-, Ge- and Sn-Mg\(_8\) clusters show similar “cage-like” geometries and are more stable than other clusters. The results of the above atomic cluster level studies show that even for homologous element-doped magnesium clusters, their structural growth is likely to be different. Therefore, the investigation of different atom-doped magnesium-based clusters is, at least theoretically, worthy of a comprehensive study. Interestingly, to the best of our knowledge, the studies on the Ga atom doped with magnesium cluster have not been reported for GaMg\(_n\) system, except for Ga\(_2\)Mg\(_n\) clusters [22]. In order to fill the research gap of single gallium atom doped magnesium clusters, this work will conduct a full study of the gas-phase GaMg\(_n^−\) (n = 2–12) clusters, including their geometrical structures, relative stability, chemical bond analysis, and electronic excitation research.

2. Computational Methods

The key point in studying the atomic clusters is to obtain their structures, and the initial isomers of GaMg\(_n^−\) (n = 2–12) clusters were searched through CALYPSO in this work [23, 24]. CALYPSO quantum chemistry computer software employs a global optimization method, which is particle swarm optimization (PSO), to conduct an efficient structure prediction. For the structures of clusters [25–28], crystals and some functional materials [29–33], CALYPSO can predict their stable or substable structures when only their chemical composition and some specific external conditions (e.g. high pressure) are required. CALYPSO sets each size of the cluster to “generation” and generates a specified number of structures based on PSO and a randomized algorithm, and then optimizes these structures to obtain their energies. As long as the number of searches is large enough, the lowest energy isomers can be found on the cluster potential energy surface. For GaMg\(_n^−\) (n = 2–12) clusters, 50 generations for each size with 20 structures are contained in each generation, and 80% of the initial guess structures are generated by PSO. For the 1000 structures obtained from GaMg\(_n^−\) clusters of each size, isomers with similar structures and energies were eliminated by the auxiliary censoring function of CALYPSO. The remaining isomers were set to different spin multiplicities (1,3,5,7), and their structures and vibrational frequencies were calculated using DFT with B3LYP functional [34, 35] and 6-311G(d) basis group [36] in Gaussian09 package [37]. The reason for choosing such functional and basis groups is that there are no metallic bonds in such a small magnesium-based cluster and several similar successful works have been reported. Vibration frequency calculations require results without imaginary frequencies, thus ensuring that the obtained isomers are true low-energy states and not excited states. If the result of an isomer calculation contains an imaginary frequency, it needs to be eliminated and recalculated until all frequencies are positive.
For the lowest-energy isomers \( \text{GaMg}_n^- \) (\( n = 2–12 \)), charge transfer and electron configuration were analyzed through natural bond orbital (NBO) computation [38]. The excited state properties were obtained by time-dependent DFT (TDDFT) calculations. Electron localization function (ELF) [39] was used to analyze the chemical bond property of \( \text{GaMg}_n^- \) (\( n = 2–12 \)). In this work, further detailed research was performed for the most stable cluster, including ultraviolet-visible absorption spectrum (UV-Vis), infrared (IR) and Raman spectra, hole-electron [40] and natural transition orbitals (NTO) [41] analysis of its electronic excitation characteristics. In addition, Multiwfn [42] and VMD [43] software were also used to analyze and plot some properties related to the wave function properties of clusters.

3. Results And Discussions

3.1 The geometrical structures of \( \text{GaMg}_n^- \) clusters

Based on the calculation method in the previous section, for each size \( \text{GaMg}_n^- \) cluster structure optimization and frequency calculation, many isomers on the potential energy surface are obtained. Since the lowest energy isomers (n-1) in the potential energy plane are relatively stable and important, these lowest energy isomers are shown in Fig. 1 and their information such as symmetry, electron state and the lowest vibrational frequency are displayed in Table 1. In addition, Fig. 1 also shows the structures and information of the second-lowest isomers (n-2) and third-lowest isomers (n-3) energy isomers together. The positive value of the lowest vibrational frequency of each ground state isomer in Table 1 follows the computational requirements and ensures that these isomers are true ground states and not excited states. For the structural growth of \( \text{GaMg}_n^- \) clusters, as shown in Fig. 1, isomers 2–1 (\( C_{2v} \), \( 3B_1 \)), 2–2 (\( C_{2v} \), \( 3A_1 \)) and 2–3 (\( C_{2v} \), \( 1A_1 \)) all show similar isosceles triangle geometry. The energy of isomer 2–2 and ground state 2–1 are equal and 0.24 eV lower than the energy of isomer 2–3. Isomers 3–1 (\( C_{3v} \), \( 1A_1 \)) and 3–2 (\( C_{3v} \), \( 3A^* \)) have tetrahedral structure and 0.01 eV energy difference. Isomer 3–3 (\( C_{2v} \), \( 1A_1 \)) shows a plane quadrilateral composed of two isosceles triangles, which is higher 0.54 eV energy than isomer 3–1. For \( \text{GaMg}_4^- \) isomers, both the ground state isomer 4–1 (\( C_{3v} \), \( 1A_1 \)) and the second-lowest isomer 4–2 (\( C_{3v} \), \( 3A^* \)) have an elongated tetrahedral structure (four Mg atoms at fixed points), but with a Ga atom inside it. By attracting an Mg atom to the left of the 3–1 isomer's Ga atom, the isomer 4–3 (\( C_2 \), \( 3B \)) is formed. Calculations show that the second and third lowest \( \text{GaMg}_4^- \) isomers are 0.01 eV and 0.03 eV higher than the ground state energy, respectively. The structure of the isomer 5–1 (\( C_{3v} \), \( 1A_1 \)) is based on the deformation of the isomer 4–1 by attracting an Mg atom, while isomers 5–2 (\( C_{3v} \), \( 1A_1 \)) and 5–3 (\( C_{3v} \), \( 3A^* \)) are deformed structures based on the tetrahedral 3–1 structure attracting two Mg atoms in different directions. The energy of the ground state isomer 5–1 is 0.05 eV and 0.07 eV lower than that of the isomers 5–2 and 5–3, respectively. The lowest energy isomer 6–1 (\( C_{3v} \), \( 1A_1 \)), which has 0.07 eV and 0.10 eV lower energy than the second and third lowest isomers, presents a pyramid-shaped deformation structure. Isomers 6–2 (\( C_1 \), \( 3A \)) and 6–3 (\( C_{2v} \), \( 1A_1 \)) have a double tetrahedral structure with Ga atom as
common vertices. Interestingly, isomers $7 - 1 (Cs, 1A')$, $7 - 2 (Cs, 3A')$, $7 - 3 (C_1, 3A)$, $8 - 1 (C_2v, 1A_1)$, $8 - 2 (Cs, 1A')$, $9 - 1 (Cs, 1A')$, $9 - 2 (C_1, 1A)$, $9 - 3 (Cs, 1A')$, $10 - 1 (C_1, 1A)$, $10 - 2 (C_1, 1A)$, $10 - 3 (C_2v, 1A_1)$, $11 - 1 (Cs, 1A')$, $11 - 2 (Cs, 1A')$, $11 - 3 (C_1, 1A)$, $12 - 1 (C_1, 1A)$ and $12 - 3 (Cs, 1A')$ all share a common pyramidal skeleton structure, which then attracts additional Mg atoms in different directions. Relative to their respective ground state isomer energies, $7 - 2$ and $7 - 1$ have the same energy, both being $0.22$ eV lower than $7 - 3$. Isomers $8 - 2$ and $8 - 3 (Cs, 1A')$ have energies $0.01$ eV and $0.49$ eV higher than the ground state. Calculations show that the second and third lowest energy isomers of the GaMg$_9^-$ cluster have energies $0.11$ eV and $0.14$ eV higher than the lowest energy isomer. For GaMg$_{10}^-$, ground state isomer $10 - 1$ is lower in energy than isomers $10 - 2$ and $10 - 3$ by $0.09$ eV and $0.21$ eV. The search of the potential energy surface of the GaMg$_{11}^-$ cluster shows that isomers $11 - 2$ and $11 - 3$ can be found at $0.20$ eV and $0.47$ eV higher than the energy of isomer $11 - 1$. Isomers $12 - 2 (C_1, 1A)$ and $12 - 3$ are confirmed to be higher in energy than the ground state energy by $0.07$ eV and $0.28$ eV.
Table 1
Symmetry, electronic state, average bonding energy ($E_b$), the second order difference energy ($\Delta_2E$), and the lowest vibrational frequency in the ground state of GaMg$_n^-$ ($n = 2–12$) clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Symmetry</th>
<th>State</th>
<th>$E_b$ (eV)</th>
<th>$\Delta_2E$ (eV)</th>
<th>Lowest Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaMg$_2^-$</td>
<td>$C_{2v}$</td>
<td>$^3B_1$</td>
<td>1.76</td>
<td>$-$</td>
<td>105</td>
</tr>
<tr>
<td>GaMg$_3^-$</td>
<td>$C_{3v}$</td>
<td>$^1A_1$</td>
<td>1.86</td>
<td>0.37</td>
<td>111</td>
</tr>
<tr>
<td>GaMg$_4^-$</td>
<td>$C_{3v}$</td>
<td>$^1A_1$</td>
<td>1.85</td>
<td>-0.12</td>
<td>22</td>
</tr>
<tr>
<td>GaMg$_5^-$</td>
<td>$C_s$</td>
<td>$^1A'$</td>
<td>1.86</td>
<td>-0.18</td>
<td>8</td>
</tr>
<tr>
<td>GaMg$_6^-$</td>
<td>$C_s$</td>
<td>$^1A'$</td>
<td>1.89</td>
<td>-0.20</td>
<td>31</td>
</tr>
<tr>
<td>GaMg$_7^-$</td>
<td>$C_s$</td>
<td>$^1A'$</td>
<td>1.94</td>
<td>-0.25</td>
<td>39</td>
</tr>
<tr>
<td>GaMg$_8^-$</td>
<td>$C_{2v}$</td>
<td>$^1A_1$</td>
<td>2.01</td>
<td>0.78</td>
<td>37</td>
</tr>
<tr>
<td>GaMg$_9^-$</td>
<td>$C_s$</td>
<td>$^1A'$</td>
<td>1.98</td>
<td>-0.04</td>
<td>19</td>
</tr>
<tr>
<td>GaMg$_{10}^-$</td>
<td>$C_1$</td>
<td>$^1A$</td>
<td>1.96</td>
<td>-0.17</td>
<td>17</td>
</tr>
<tr>
<td>GaMg$_{11}^-$</td>
<td>$C_s$</td>
<td>$^1A'$</td>
<td>1.97</td>
<td>0.21</td>
<td>37</td>
</tr>
<tr>
<td>GaMg$_{12}^-$</td>
<td>$C_1$</td>
<td>$^1A$</td>
<td>1.95</td>
<td>$-$</td>
<td>10</td>
</tr>
</tbody>
</table>

Summarily, the above studies at the atomic cluster level have shown that doping of magnesium clusters with $-1$ valence gallium atom results in the formation of various structures with little difference in energy between the ground state isomers and other low energy isomers. It is found that, at least in the medium size, two important structures, the tetrahedral-based GaMg$_3^-$ to GaMg$_5^-$ and the pyramidal-based GaMg$_6^-$ to GaMg$_{12}^-$ were found to be the "seeds" of their growth. This structure growth mechanism of magnesium-based clusters has been reported in other studies, such as BeMg$_n$ [14, 17, 28], SiMg$_n$ [19], SrMg$_n$ [12], GeMg$_n$ [21], etc. Among these structures, the ground state GaMg$_6^-$ stands out due to its high symmetry and complete pyramidal-like structure.

3.2 The relative stabilities
The size-dependent property of the cluster structures determines that their relative stability is worth investigating. The relative stability of the ground state isomers of each size in Fig. 1 is fully studied in this section. For the convenience of researchers, information on the atomic coordinates of these ground-state structures is shown in Table S1 of the Supplementary Material. As Eqs. (1)-(5) shown below, three energies that can determine the cluster stability are calculated here, namely, the average binding energy ($E_b$), the second-order energy difference ($\Delta_2 E$), and several energy gaps ($E_{\text{gap}}$).

$$E_b(GaMg_n^-) = \frac{nE(Mg) + E(Ga^-) - E(GaMg_n^-)}{n+1}$$  \hspace{1cm} (1)

$$\Delta_2 E(GaMg_n^-) = E(GaMg_{n+1}^-) + E(GaMg_{n-1}^-) - 2E(GaMg_n^-)$$  \hspace{1cm} (2)

$$E_{\text{HOMO-LUMO Gap}} = E_{\text{LUMO}}(GaMg_n^-) - E_{\text{HOMO}}(GaMg_n^-)$$  \hspace{1cm} (3)

$$E_{\text{Fundamental Gap}} = E_{\text{VIP}}(GaMg_n^-) - E_{\text{VEA}}(GaMg_n^-)$$  \hspace{1cm} (4)

$$E_{\text{Optical Gap}} = E_{s1}(GaMg_n^-) - E_{s0}(GaMg_n^-)$$  \hspace{1cm} (5)

In Eqs. (1) and (2), $E$ corresponds to the energy of each cluster or atom, $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ in Eq. (3) are the corresponding cluster energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. $E_{\text{VIP}}$ and $E_{\text{VEA}}$ in Eq. (4) are the vertical ionization potential (VIP) energy and vertical electron affinity (VEA) energy of the isomer. The $E_{s1}$ and $E_{s0}$ in Eq. (5) are the excited and ground-state energies of the isomer, and the energies are obtained from the ground state isomer in TDDFT theory. The results of these energy calculations for the ground state isomers of GaMg$_n^-$ ($n = 2–12$) are presented in Tables 1 and 2. Figure 2, on the other hand, plots their size-dependent properties.
Table 2

| Cluster | HOMO-LUMO Gap (eV) | Fundamental Gap (eV) | Optical Gap (eV) | NCP on Ga (in |e|) | NEC on Ga (in |e|) |
|---------|-------------------|---------------------|----------------|----------------|----------------|
| GaMg₂⁻  | 1.29              | 3.90                | 0.12           | -0.85          | [core]4S¹.834p².00 |
| GaMg₃⁻  | 1.23              | 3.63                | 0.66           | -0.99          | [core]4S¹.794p¹.88 |
| GaMg₄⁻  | 1.09              | 3.31                | 0.52           | -1.18          | [core]4S¹.774p².40 |
| GaMg₅⁻  | 1.05              | 3.16                | 0.42           | -1.54          | [core]4S¹.734p².00 |
| GaMg₆⁻  | 1.15              | 3.32                | 0.48           | -1.36          | [core]4S¹.714p².58 |
| GaMg₇⁻  | 1.22              | 3.38                | 0.53           | -1.27          | [core]4S¹.674p².41 |
| GaMg₈⁻  | 1.85              | 3.95                | 1.25           | -1.02          | [core]4S¹.624p².22 |
| GaMg₉⁻  | 1.68              | 3.60                | 1.12           | -1.61          | [core]4S¹.574p³.10 |
| GaMg₁₀⁻ | 1.55              | 3.47                | 1.00           | -1.74          | [core]4S¹.604p².79 |
| GaMg₁₁⁻ | 1.52              | 3.47                | 0.93           | -1.61          | [core]4S¹.524p³.15 |
| GaMg₁₂⁻ | 1.48              | 3.33                | 0.90           | -1.64          | [core]4S¹.514p³.02 |

The higher the average binding energy of the cluster, the more strongly the atoms of the cluster are bound, and thus the more stable the cluster is. As shown in Fig. 2(a), The \( E_b \) curve of the lowest energy isomer increases overall as the cluster size increases, with a local maximum value of 2.01 eV at GaMg₈⁻ and GaMg₂⁻ possessing a minimum value of \( E_b = 1.76 \) eV. This result indicates that as the cluster size increases, the cluster is more stable overall, but locally, GaMg₈⁻ is more stable than the other clusters. Figure 2(b) shows the size-dependent curve of the \( \Delta_2 E \) curve, which is a physical measure of the relative stability of clusters to their neighbors. Interestingly, the GaMg₈⁻ cluster has the largest \( \Delta_2 E \) value (0.78 eV), implying that it is more stable than the other clusters. There are three curves in Fig. 2(c), which are the HOMO-LUMO energy gap, fundamental energy gap, and optical energy gap of the cluster, respectively. These energy gaps can characterize clusters such as chemical stability and photostability. The first 50 excited states of each ground state isomer were calculated by the TDDFT method to obtain their S1
excitation energies. The calculations show that the three energy gap curves of the GaMg\textsubscript{n}\textsuperscript{−} (n = 2–12) ground state isomers have similar size trends, but surprisingly, the local peaks of the three curves appear at GaMg\textsubscript{8}−, indicating that it possesses the highest chemical and photostability compared to the other clusters. In addition, Figure S1 of the Supplementary Material demonstrates the molecular orbitals (MO) of the LUMO and HOMO energy levels of each isomer. As the cluster size increases, the effect of Ga atoms on MO becomes smaller.

In summary, based on the above discussions about energies of the lowest energy isomers of GaMg\textsubscript{n}− (n = 2–12) clusters, one can safely conclude that GaMg\textsubscript{8}− possesses the strongest local stability and thus can be considered a candidate for the "magic" cluster. In addition, this result agrees with the previous results of SiMg\textsubscript{8}−/+ [44], GeMg\textsubscript{8}+ [45], and CMg\textsubscript{8} [21] studies.

### 3.3 Charge transfer property

The study of charge transfer and electronic configuration of clusters helps to understand their electronic structure properties. By NBO calculations for the ground state isomers of GaMg\textsubscript{n}− (n = 2–12), Table 2 and Table S2 in the Supplementary Material show all charge and electronic configurations. Figure 3 displays the natural population charge (NCP) on Ga and Mg atoms, with a color rendering of charged atoms (blue and red mean gain and loss electrons, respectively). Calculations show that in all the ground state isomers of GaMg\textsubscript{n}− (n = 2–12) clusters, Ga atoms gain electrons in the range of -0.85 to -1.74 |e|, while most Mg atoms lose electrons, i.e., electrons are transferred from Mg to Ga atoms in the clusters. Specifically, there are 53 Mg atoms with positive charges ranging from 0.01 to 0.28|e|, while 24 Mg atoms with negative charges ranging from -0.01 to -0.42|e|. The electronegativity of Mg atom is 1.2, while Ga atom is 1.6. Obviously, when Ga is doped with Mg\textsubscript{n} clusters, Ga atom is easier than Mg atom to attract electrons.

Table 2 and Table S3 in the Supplementary Material also display natural electron configuration (NEC) on Ga and Mg atoms for the lowest energy isomers of GaMg\textsubscript{n}− (n = 2–12). Figure 4, on the other hand, plots their NEC in different valence orbitals. Comparing the electronic configuration of the bare Ga atom [core] 4S\textsuperscript{2}4p\textsuperscript{1}, all Ga atoms of the GaMg\textsubscript{n}− (n = 2–12) cluster ground state isomer are losing electrons in the 4S orbital, while all 4p orbitals are gaining electrons. In contrast, the electronic configuration of the bare Mg atom is [core]3S\textsuperscript{2}, and calculations show that all Mg atoms lose electrons in the 3S orbital and gain electrons in the 3p orbitals. Numerically shown in Fig. 4(a), the loss of electrons from the 4S orbitals of Ga atoms shows an overall increasing trend as the cluster size increases, ranging from 0.49 to 0.17 |e|. The 4p orbitals of Ga atoms gain electrons ranging from 0.88 to 2.15 |e|. Figures 4(b) and (c) show the NEC distribution of Mg atoms in different sizes, and their values are related to structural symmetry. Apparently, NEC calculations indicate that in the GaMg\textsubscript{n}− cluster, the 4s→4p electron transfer occurs in the orbitals of the valence layer of the Ga atom, while the 3s→3p electron transfer occurs in the Mg atoms.
3.4 The chemical bond property analysis through ELF

At the atomic cluster level, the chemical bonding properties of clusters are very interesting objects to study because they can help researchers gain insight into the changes in the interactions during atomic aggregation. For example, one of the scientific questions in the study of magnesium-based clusters is to investigate at what size does the metallicity of the Mg-Mg bond emerge? However, previous studies have shown that Mg-Mg is bonded in the covalent form in the small size (at least less than 20 Mg atoms) magnesium-based clusters [13, 14, 16, 20, 22]. The electron localization function (ELF) is always used to study the covalent bonds in the cluster [39]. ELF is a three-dimensional real space function with values ranging from 0 to 1. In general, the electrons in the regions with higher ELF values (always ≥ 0.5) are strongly localized, while those in the regions with lower ELF values are weakly localized. The electrons are covalently bonded in the high-ELF region, while they are non-covalently bonded in the low-ELF region. Figure 5 and Figure S2 in the Supplementary Material show the ELF 2D diagrams of all the ground state isomers of the GaMg$_n^-$ (n = 2–12) clusters. The ELF calculations show that Mg-Mg covalent bonds appear from GaMg$_2^-$ to GaMg$_{12}^-$. This result differs from other Mg-based cluster studies, such as the PdMg$_7$ [20] and AuMg$_4$ [13] clusters where Mg-Mg covalent bonds start to appear. This is probably because Ga atom, unlike Au and Pd atoms, are unable to "break up the Mg atoms far enough" when doping Mg clusters. In addition, the ELF values around Ga atoms indicate that Ga-Mg bonding is non-covalent and when considering electron transfer analysis in the previous section, Ga-Mg bonds can be regarded as ionic bonds.

3.5 UV-Vis, IR and Raman spectra of GaMg$_8^-$ cluster

The ground state isomer of the GaMg$_8^-$ cluster was shown to be the most stable in the relative stability analysis section, indicating that it has the highest probability of being observed experimentally (although there is no experimental support for it at present). Therefore, it is interesting to make some theoretical predictions for future possible experimentally spectra. Figure 6 presents the ultraviolet-visible absorption spectrum (UV-Vis), infrared (IR) and Raman spectra of the GaMg$_8^-$. The first 50 excited states of GaMg$_8^-$ were calculated in the TDDFT method to obtain its excitation energy and oscillator strengths, and were employed to simulate the UV-Vis absorption spectrum, as displayed in Fig. 6(a). Calculations show that all absorption peaks have very small (near zero) oscillator strength, so the focus here is on the information of the strongest absorption peak, which is located at 544 nm with an oscillator strength of 0.04. In addition, calculations further confirm that the strongest absorption peak originated from the contribution of S0→S6, S0→S12, S0→S19, and S0→S26 excitations. Another important conclusion of Fig. 6(a) is that seven of the eight distinct absorption peaks with a low value of oscillator strength are in the visible region (380–760 nm), indicating that the GaMg$_8^-$ cluster is colored but not easily observable.

The theoretical predictions of the IR and Raman spectra of GaMg$_8^-$ cluster are displayed in Fig. 6(b). Infrared and Raman spectra are related to the structure of the clusters, so this theoretical calculation is useful for experimental observations. As shown in Fig. 6(b), for the IR spectrum, one can find that there
are total of 10 strong absorption peaks in the distribution of 40–250 cm\(^{-1}\). The strongest IR peak is located at 219 cm\(^{-1}\) with the symmetric stretching vibrations of Ga1-Mg2, Ga1-Mg6, Ga1-Mg5 and Ga1-Mg9. For Raman spectrum, two distinct strong peaks and seven relatively weak Raman peaks can be found, with the strongest peak appearing at 182 cm\(^{-1}\). The cluster vibration corresponding to the strongest Raman peak is a breathing vibration mode centered on Ga1. Obviously, for the GaMg\(_8^-\) cluster, the strong peaks of IR spectra are relatively numerous and narrowly distributed, which is more difficult for direct observation than Raman spectrum.

### 3.6 Excited-state analysis of GaMg\(_8^-\) cluster via hole-electron and NTO

Since the UV-Vis of the GaMg\(_8^-\) cluster in Fig. 6(a) reveals significant contributions to the spectrum from four excited states, S6, S12, S19 and S26, it is interesting to analyze these four excited states via hole-electron [40,46] and NTO [41]. The hole-electron theory can be used to analyze arbitrary excitations of the system, since it will give an unambiguous picture of the distribution of holes and electrons, describing the positions where the excited electrons leave and arrive. Since the hole-electron analysis is such a powerful method for revealing the nature of electron excitations, it has been adopted in many recent studies [40,47–50]. As presented in Fig. 7, in the process of S0\(\rightarrow\)S6, S0\(\rightarrow\)S12, S0\(\rightarrow\)S19, and S0\(\rightarrow\)S26, the hole-electron distribution does not differ much. Specifically, the leaving electrons are mainly from Mg2, Mg6, Mg5 and Mg9 which can bond with Ga atoms, (see Fig. 6(b)). This indicates that in states S1, S6, S16 and S26, both Mg-Mg and Ga-Mg are involved in the excitation.

Here we also do the NTO analysis of the above excited states, which can further help us to understand the orbital transition contribution. As shown in Fig. 8 and Figure S3 in the Supplementary Material, for the S6, S12, S19 and S26 states, the NTO64\(\rightarrow\)NTO65 transition make the largest contribution to the electronic excitation with 96.18%, 55.01%, 38.42% and 35.67%, respectively. In addition, NTO62\(\rightarrow\)NTO67 of S19 and S26, NTO63\(\rightarrow\)NTO66 of S12, S19 and S26, In addition, the second most significant electronic excitation contribution to the S12, S19 and S26 states is the NTO63\(\rightarrow\)NTO66 transition, accounting for 43.29%, 35.20% and 35.26%, respectively. Finally, the contributions of the NTO62\(\rightarrow\)NTO67 transition to the electronic excitation of the S19 and S26 states are also quite large, which are 23.36% and 20.42%, respectively.

### 4. Conclusions

In conclusion, based on the atomic cluster level study motivation, the present work provides a systematic theoretical study of -1 valent Ga atom doped magnesium, GaMg\(_n^-\) (n = 2–12) clusters. The structural growth mechanism of GaMg\(_n^-\) clusters has confirmed that tetrahedral-like and pyramidal-like structures are the two "seeds" of their growth. Various energy stability calculations show that GaMg\(_8^-\) cluster has the highest stability and is a candidate for the "magic" cluster. Studies of charge transfer properties indicate that Ga atom always gains electrons while most Mg atoms play the role of losing electrons. NEC
calculations further reveal that the electron transfer within the valence orbitals of Ga and Mg atoms during cluster formation is s→p. ELF analysis yielded that Mg-Mg is covalently bonded in all clusters starting from GaMg$_2^-$, as well as Ga-Mg is ionically bonded. Furthermore, UV-Vis, IR and Raman spectroscopic predictions were also performed specifically for the most stable cluster GaMg$_8^-$, and the excited state properties of this cluster were investigated by the hole-electron method as well NTO.

**Declarations**

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Figures
Figure 1

The three low-energy isomers structures of GaMg$_n$\(^{+}\) (n=2-12) clusters, and the energy difference (in eV) compare to the ground state.
Figure 2

Energies: (a) $E_b$, (b) $\Delta_2 E$, (c) $E_{\text{gap}}$ for HOMO-LUMO, fundamental and optical in the ground state of GaMg$_n^-$ (n=2-12) clusters.
Figure 3

NCP on Ga atom in the ground state of GaMg$_n^-$ (n=2-12) clusters.
Figure 4

NEC on (a) Ga atom (b) Mg -3S, (c) Mg-3p in the ground state of GaMgₙ⁻ (n=2-12) clusters.
Figure 5

The ELF analysis on the ground state isomer GaMg$_8^-$ cluster.
Figure 6

(a) Simulated UV-Vis absorption spectrum, (b) Theoretical predication IR and Raman spectrum for the ground state isomer GaMg$_8^-$ cluster.
Figure 7

Real space representation of hole and electron distributions of the ground state isomer GaMg₈⁻ cluster for S₀→S₆, S₀→S₁₂, S₀→S₁₉ and S₀→S₂₆ excitation.
Figure 8

NTO analysis on the ground state isomer of GaMg$_8^-$ cluster for S0→S6, S0→S12, S0→S19 and S0→S26 excitation.

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