Computational Exploration on the Structural and Optical Properties of Gold-Doped Alkaline-Earth Magnesium AuMg_n (n = 2–12) Nanoclusters: DFT Study

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Using CALYPSO crystal search software, the structural growth mechanism, relative stability, charge transfer, chemical bonding and optical properties of AuMg_n (n = 2–12) nanoclusters were extensively investigated based on DFT. The shape development uncovers two interesting properties of AuMg_n nanoclusters contrasted with other doped Mg-based clusters, in particular, the planar design of AuMg3 and the highly symmetrical cage-like of AuMg9. The relative stability study shows that AuMg10 has the robust local stability, followed by AuMg9. In all nanoclusters, the charge is transferred from the Mg atoms to the Au atoms. Chemical bonding properties were confirmed by ELF analysis that Mg-Mg formed covalent bonds in nanoclusters larger than AuMg3. Static polarizability and hyperpolarizability calculations strongly suggest that AuMg9 nanocluster possesses interesting nonlinear optical properties. Boltzmann distribution weighted average IR and Raman spectroscopy studies at room temperature verify that these nanoclusters are identifiable by spectroscopic experiments. Finally, the average bond distance and average nearest neighbor distance were fully investigated.

Keywords: calypso, DFT, AuMgn nanoclusters, optical properties, structural property

INTRODUCTION

Metal nanoclusters have attracted increasing interest from academics in recent years due to their appealing micro patterns and interesting features (Jin et al., 2016; Peng et al., 2018; Tew et al., 2018). For example, Au_n clusters tend to exhibit 2-dimensional structures at small sizes, while medium sizes (n < 15) will transition to 3-dimension (Idrobo et al., 2007; Assadollahzadeh and Schwerdtfeger, 2009; Huang and Wang, 2009). For larger size, the study of Au144 cluster is highly worth explaining. It was first reported in 1997 as a critical size for the transformation of Au nanoclusters into nanocrystals and worthy of being researched, but its structure could not be determined at that time (Alvarez et al., 1997), then in 2009 it was precisely predicted by theoretical studies to have a multishell structure (Qian and Jin, 2009), and finally, in 2018 it was experimentally confirmed to have a three-layer metallic core of Au12-Au42-Au60 from the inside out (Yan et al., 2018). Researchers have been so persistent in studying them because the physical size of these clusters is comparable to the electron Fermi wavelength and therefore tends to show interesting electronic (Yau et al., 2013), optical properties (Ramakrishna et al., 2008; Jin, 2015) and have important application prospects in the field of medicine and biology (Shang et al., 2011). Because the physical and chemical characteristics of
nanoclusters alter with size throughout the transition to nanocrystals or nanoparticles, nanocluster research will anticipate, at least theoretically, a slew of new materials for the field of nanomaterials science.

A lot of studies on alkaline Earth metal magnesium clusters have been reported, in addition to usual studies of metal nanoclusters like gold, silver, and copper (Köhn et al., 2001; Xia et al., 2016; Zhang et al., 2020; Zhao et al., 2021). This is partly because magnesium-based nanomaterials have an exceptional hydrogen storage capacity compared to ordinary materials (Shao et al., 2012), and therefore, various kinds of Mg-based nanocluster materials, such as CoMg₈ (Trivedi and Bandyopadhyay, 2015), RhMg₄ (Trivedi and Bandyopadhyay, 2016), ScMg nanocluster (Chen et al., 2020; Lyon, 2021), are worthy of systematic study. Most of these studies were carried out theoretically and gave interesting results by predicting the hydrogen storage properties of nanocluster materials based on Mg. For example, it is shown that MgScH₁₃ and MgScH₁₅ nanoclusters have, theoretically, ultra-high hydrogen storage capacities of 15.9 wt% (Lyon, 2021) and 17.8 wt% (Chen et al., 2020), respectively. On the other hand, the optical properties of Mg and Mg-based nanoclusters are also very attractive (Belyaev et al., 2016; Shinde, 2016; Shinde and Shukla, 2017). The IR spectra of Mgₙ (n = 2–31) nanoclusters were studied using DFT, and the results showed that their most intense peaks were distributed in the low-frequency band of 40–270 cm⁻¹ (Belyaev et al., 2016). The linear absorption spectroscopy studies of very small size Mgₙ (n = 2–5) nanoclusters confirm that their low-lying structures, although small, can be experimentally distinguished, while the optical excitation spectra are confirmed to be of plasmonic collective type (Shinde, 2016).

In short, nanocluster materials, like Au and Mg, are a field of materials science full of unknown “surprises” where many interesting optical and electronic excitation properties can be “discovered”. However, surprisingly, the study of gold-doped Mg nanoclusters has not been reported so far. This work aims to perform a systematic computational study of the structural and optical properties of gold-doped small-size magnesium nanoclusters. Specifically, the geometric growth mechanism, relative stability, charge transfer properties, chemical bonding properties, nonlinear optical properties, and theoretical calculations of infrared and Raman-weighted average spectra of AuMgₙ (n = 2–12) nanoclusters will be investigated. These studies will not only enrich the research data on AuMgₙ nanoclusters, but also provide the opportunity to gain insight into potential nanomaterials with interesting optical properties.

**COMPUTATIONAL METHOD DETAILS**

CALYPSO software (Wang et al., 2010, 2012) was utilized to search the initial geometries of AuMgₙ (n = 2–12) nanoclusters. CALYPSO can perform predictions of the energetically low-lying isomers structures at given chemical compositions and pressure for nanoclusters (Lv et al., 2012; Zhao et al., 2019; Lu et al., 2020) in gas-phase and crystals (Lu and Chen, 2020a, 2020b, 2021; Sun et al., 2020; Chen et al., 2021) via particle swarm optimization (PSO) algorithm. To search for as many low-lying energy isomers of AuMgₙ (n = 2–12) nanoclusters as possible, the following strategy will be employed. First, each size of AuMgₙ nanocluster will be searched for 50 generations, where each generation contains 20 structures. Further, 80% of these 1,000 heterogeneous structures are generated by the PSO algorithm for the initial structure, and the rest are generated randomly. These structures are then interfaced via CALYPSO to Gaussian 09 software (Frisch et al., 2016) for low-level HF energy calculations, and finally ranked by energy level. It is necessary to explain that many of the 1,000 isomers obtained have the same or extremely close energies, and their geometrical structures do

![FIGURE 1 | The geometry of the three lowest energy isomers of AuMgₙ (n = 2–7) nanoclusters, energy difference in eV from the lowest energy isomer at the same size.](image-url)
not differ much and therefore need to be removed. Finally, isomers with significantly different energies and structures were again subjected to high-level DFT for structural optimization and frequency calculations by Gaussian 09 software. The structure optimization calculation employs the classical B3LYP functional, where the mixed basis set is considered due to the presence of Au atom. Concretely, 6–311g(d) is applied to Mg atoms, while the pseudopotential basis set lanl2dz is used for Au atoms. The adoption of such functional and basis set is based on the following two aspects, firstly, the existing studies have shown that Mgₙ nanoclusters do not have any metallic properties at the size of n < 20 (Köhn et al., 2001; Jellinek and Acioli, 2003; Xia et al., 2016), and secondly, all-electron basis set and lanl2dz basis set have been proved to be reliable for Mg and Au nanoclusters by numerous studies (Xia et al., 2016; Zeng et al., 2020; Zhu et al., 2021). To ensure a more comprehensive structural optimization, each isomer was calculated under 2, 4, 6, and 8 spin multiplicities, respectively. In addition, to verify that the isomer is not a transition or excited state, imaginary frequencies must be excluded from any result. Once the imaginary frequency appears in the calculation result, they need to be optimized again until all frequencies are positive. Charge transfer property of the lowest energy AuMgₙ (n = 2–12) nanoclusters was analyzed by natural bond orbital (NBO) calculation (Reed et al., 1988). Chemical bonding properties were computed through the electron localization function (ELF) (Becke and Edgecombe, 1990). The nonlinear optical properties of the ground state AuMgₙ nanoclusters were investigated at the aug-cc-pVTZ level. Infrared and Raman spectra are the results of vibration frequency calculations. In particular, Multiwfn software (Lu and Chen, 2012) is a powerful tool to draw 2D map of ELF, spherical plots of static and super-static polarizabilities, Boltzmann distribution probabilities of different isomers and weighted average IR and Raman spectral data.

RESULTS

The Geometrical Growth Mechanism of AuMgₙ Nanoclusters

The growth mechanism of nanoclusters can be studied by their geometric structures. Three low-lying energy isomers of each size AuMgₙ (n = 2–12) nanoclusters are presented in Figure 1 and Figure 2. Under each structure, the “i” in AuMgₙ-i is their energy order, with “1” indicating the lowest and “2” the second-lowest ones. The energy difference (eV) between the AuMgₙ-i and AuMgₙ-1 at each size can also be found. In addition to the symmetry, and the electronic structure information is also shown in Figures 1, 2. All information about the lowest energy state of AuMgₙ (n = 2–12) nanoclusters is summarized in Table 1, where the results of the frequency calculations show the lowest and highest vibrational frequencies satisfying the requirements that the results of the frequency calculations cannot contain any imaginary frequency. As can be seen from Figure 1, isomers AuMg₂-1 (Dₐₙₙ symmetry with ²Σ⁺ electronic state) and AuMg₂-2 (C₂ᵥ symmetry with ²Σ⁺ electronic state) have a similar linear structure, the difference being that the Au atom is in the center of the former and on the side of the latter. Isomers AuMg₂-3(C₂ᵥ symmetry with ²B₂ electronic state) show a 2D planar isosceles triangle structure. Relative to the lowest energy state AuMg₂-1 isomer energy, AuMg₂-2 and AuMg₂-3 isomers have 0.24 and 0.39 eV higher energy than it, respectively. The isomer AuMg₃-1 (Dₘₙₙ symmetry with ²A¹ electronic state) has an equilateral triangular geometry, while the isomer AuMg₃-2 (C₂ᵥ symmetry with ²A¹ electronic state) has an isosceles triangular structure, and interestingly the Au atoms are located at the center of their triangular structures, respectively. The structure of the isomer...
AuMgₙ₋₂ (C₂ᵥ symmetry with 2A₁ electronic state) is a planar combination of Au-Mg-Mg isosceles triangle and Mg-Mg-Mg isosceles triangle. Calculations show nanoclusters of 2 Mg atoms doped with one Au atom, where the second and third lowest isomers are 0.03 and 4.20 eV higher than the lowest energy isomer, respectively. The structures of the isomers AuMgₙ₋₁ (C₢ᵥ symmetry with 2A₁ electronic state) and AuMgₙ₋₂ (C₂ᵥ symmetry with 2A₁ electronic state) can be considered as formed based on the tetrahedral (pyramid-like) structure of Au-Mg-Mg-Mg adsorbing an Mg atom in different directions. The isomer AuMgₙ₋₃ (C₂ᵥ symmetry with 2B₁g electronic state) shows a rectangular structure in which the 4 Mg atoms are at the vertices while Au atom is at the geometric center. For the isomer AuMgₙ₋₁, AuMgₙ₋₂ and AuMgₙ₋₃ are higher in energy by 0.01 and 0.49 eV, respectively. The structure of the isomer AuMgₙ₋₁ (C₢ᵥ symmetry with 2A₁ electronic state) is based on the formation of AuMgₙ₋₂ by adsorbing an Mg atom on its top. The isomers AuMgₙ₋₂ and AuMgₙ₋₁ form the isomers AuMgₙ₋₁ (C₢ᵥ symmetry with 2A₁ electronic state) and AuMgₙ₋₂ (C₢ᵥ symmetry with 2A₁ electronic state) after pulling up the Au atom into the interior of the polyhedral while adsorbing an Mg atom on their tops. The second- and third-lowest energy isomers of the AuMgₙ nanocluster are 0.08 and 0.16 eV higher than the lowest energy isomer, respectively. The structures of the isomers AuMgₙ₋₁ and AuMgₙ₋₂ have the same symmetry (C₢ᵥ), electronic structure (2A₁), energy and “fascinating cage-like” structures. The isomer AuMgₙ₋₃ (2A’ electronic state), which is 0.08 eV higher in energy than AuMgₙ₋₁, has a cage-like structure with C₁ symmetry. The structures of the isomers AuMgₙ₋₁ (C₢ᵥ, symmetry with 2A₁ electronic state) and AuMgₙ₋₂ (C₢ᵥ symmetry with 2A electronic state) are easily obtained by the deformation of AuMgₙ₋₁ by adsorption of an Mg atom. On the other hand, AuMgₙ₋₁ (C₢ᵥ symmetry with 2A’ electronic state) is formed by the deformation of AuMgₙ₋₁ by adsorption of an Mg atom. AuMgₙ₋₂ and AuMgₙ₋₃ have higher energies than AuMgₙ₋₁ at 0.03 and 0.39 eV. The isomer AuMgₙ₋₁ (C₢ᵥ symmetry with 2A’ electronic state) is generated based on the deformation of AuMgₙ₋₃ after adsorption of an Mg atom, while the structure of the isomer AuMgₙ₋₂ (C₁ symmetry with 2A’ electronic state) can be obtained from the deformation of AuMgₙ₋₂ by adsorption of an Mg atom. The second and third lowest energy isomers of AuMgₙ nanoclusters are higher in energy than the ground state by 0.01 and 0.17 eV. The isomers AuMgₙ₋₁ and AuMgₙ₋₂ have the same symmetry (C₢ᵥ), electronic structure (2A₁), energy and “fascinating cage-like” structures. 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adsorption of Mg atoms in different directions, and the interesting point is that the direction of adsorption does not have a fixed pattern. Such result is consistent with many existed Mg-based nanoclusters reported (Li et al., 2017; Zeng et al., 2020, 2021; Zhu et al., 2020). However, despite the many similarities, the structures of gold-doped Mg nanoclusters have unique properties compared to other Mg-based nanoclusters studies. For example, the structure of AuMg$_3$ nanoclusters is 2D planar, while the lowest energy heterostructures of Be (Zeng et al., 2020), Si (Zhu et al., 2020), C, Ge, Sn (Zeng et al., 2021), Zn-doped (Li et al., 2017) Mg nanoclusters of corresponding sizes are all ortho-tetrahedral in shape. Interestingly, although the ground-state structures of AuMg$_9$ and BeMg$_9$ (Zeng et al., 2020) look similar, the significant difference between them is that the Au atom locates on the surface of AuMg$_9$ while the Be atom is absorbed into the inside of BeMg$_9$.

The Relative Stabilities

Since clusters exhibit different physical and chemical properties at different sizes, their relative stability is well worth studying. The relative stability of cluster can be calculated through the following three quantities, that is the binding energy per atom ($E_b$ in eV), the second-order energy difference ($\Delta_2 E$ in eV) and the HOMO-LUMO energy gap ($E_{\text{gap}}$ in eV). Equations 1–3 display the above three energies for AuMg$_{n-1}$ ($n = 2$–$12$) nanoclusters in Figure 1.

$$E_b (\text{AuMg}_n) = \left[ nE (\text{Mg}) + E (\text{Au}) - E (\text{AuMg}_n) \right] / (n + 1)$$  \hspace{1cm} (1)

$$\Delta_2 E (\text{AuMg}_n) = E (\text{AuMg}_{n+1}) + E (\text{AuMg}_{n-1}) - 2E (\text{AuMg}_n)$$  \hspace{1cm} (2)

$$E_{\text{gap}} (\text{AuMg}_n) = E_{\text{LUMO}} (\text{AuMg}_n) - E_{\text{HOMO}} (\text{AuMg}_n)$$  \hspace{1cm} (3)

$E (\text{Au})$ and $E (\text{Mg})$ denote the energies of free Au and Mg atoms, $E (\text{AuMg}_n)$ means the energy of the corresponding nanocluster. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies are $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$.

The theoretically calculated values of these quantities for AuMg$_{n-1}$ ($n = 2$–$20$) nanoclusters are presented in Table 1 and their curves with size are showed in Figure 3. As Figure 3A displayed, overall, the $E_b$ curve becomes larger as the size of the nanoclusters increases, implying that the atoms within the AuMg$_n$ nanoclusters bind more stably as the Au atoms are doped. Locally, the maximum value of $E_b$ appears at AuMg$_{10}$ (1.90 eV), indicating that this nanocluster has the robust stability. Secondly, a small local peak (1.84 eV) appears at AuMg$_9$, indicating that it is slightly more stable than its neighbors. Figure 3B shows the curve of the $\Delta_2 E$, which can be detected experimentally by mass spectrometry. Interestingly, as in the case of the local peaks of the $E_b$ curve, AuMg$_9$ and AuMg$_{10}$ have local maximum $\Delta_2 E$ values of 0.29 and 0.28 eV, respectively. This conclusion suggests that they are both the most stable and have a high probability of being observed in mass spectrometry experiments. The thermodynamic stability of nanoclusters can be characterized by the value of their $E_{\text{gap}}$. Since AuMg$_n$ nanoclusters are open-shell systems, they have both $\alpha$ and $\beta$-electrons, and the $E_{\text{gap}}$ of $\alpha$ and $\beta$-electrons are illustrated in Figure 3C and Figure 3D. For $\alpha$-electrons $E_{\text{gap}}$ curve of AuMg$_n$ nanoclusters, the local peaks appear at $n = 5$, 9 and 11, while AuMg$_{10}$ has the largest local $\beta$-electron $E_{\text{gap}}$ indicating that the thermal stability of these clusters is relatively high.

In conclusion, AuMg$_9$ and AuMg$_{10}$ nanoclusters show the robust stability. However, it is noteworthy that the AuMg$_9$
nanocluster is always the second largest value in both $E_b$ and $\Delta_2E$ curves, although they are not the maximum values. Therefore, combined with the $E_{\text{gap}}$ maximum for $\alpha$-electrons, AuMg$_9$ nanocluster also has considerable robust stability and be worthy studying.

**Charge Transfer Property and Chemical Bond Analysis**

The natural charge population (NCP) results from the NBO calculations can reveal the charge transfer properties in the nanoclusters. The NCP values of Au atoms in Table 1 are in the range of $[−2.99, −0.74]$ e, indicating that Au atoms play the role of electron receiver in all nanoclusters. The curve of NCP on Au atom with the size is plotted in Figure 4. The AuMg$_9$ nanocluster appears to be very special, which is probably originated from its high symmetry structure. Supplementary Table S2 in the Supplementary Material shows the NCP values on the Mg atoms. Except for 4 Mg atoms in AuMg$_9$ with a charge of −0.05 e and 1 Mg atom in AuMg$_{12}$ with an NCP value of −0.01 e, all other Mg atoms have positive NCP values, distributed from 0.65 to 0.01 e, suggesting that they are losing electrons. In other words, Mg atoms are electron donors in the AuMg$_n$ nanoclusters. The charge transfer property depends on the electronegativity of the atom, the greater the electronegativity, the easier it is to get electrons. The electronegativity value of Mg atom is 1.31, while that of Au atom is 2.54, so the charge transfer is mostly from Mg atom to Au atom.

The ELF values of atomic bonding regions and their 2D maps are useful tools for analyzing the chemical bonding properties of nanoclusters. ELF is a value greater than 0 and less than 1, which characterizes the degree of electron localization and thus can determine the bonding properties. A region with ELF $>0.5$ implies high electron localization and covalent bonding in the bonding region, while a region with ELF $<0.5$ has low electron localization and non-covalent bonding in the bonding region.

**The Nonlinear Optical Property**

Static polarizabilities $\alpha(\infty)$ and hyperpolarizabilities $\beta(\infty)$ for the ground state AuMg$_n$ ($n = 2−20$) nanoclusters were calculated to analyze their nonlinear optical property. Specifically, the coupled-perturbed Kohn-Sham (CPKS) method (Jensen, 2017) was adopted for the AuMg$_n$ nanoclusters to compute the polarizabilities and hyperpolarizabilities in the zero-frequency limit ($\lambda \rightarrow \infty$). The results of $\alpha(\infty)$ and $\beta(\infty)$ calculations are presented in Supplementary Table S3 in the Supplementary Material and are shown in Figure 6. From Figure 6A, it can be seen that the polarization anisotropy $\alpha_{\text{aniso}}(\infty)$ and isotropy $\alpha_{\text{iso}}(\infty)$ of AuMg$_n$ nanoclusters do not change consistently with the size. The $\alpha_{\text{iso}}(\infty)$ shows an overall upward trend, except for AuMg$_9$, while the $\alpha_{\text{aniso}}(\infty)$ oscillates with increasing size. In addition, $\alpha_{xx}(\infty)$, $\alpha_{yy}(\infty)$, $\alpha_{zz}(\infty)$ of each nanocluster are also shown in Figure 6A. Due to the diversity of the nanoclusters structures, these quantities display irregular oscillations in different directions. However, AuMg$_9$ nanocluster with high structural symmetry exhibits synchronous local minimum anisotropic and isotropic polarization, suggesting that it has special nonlinear optical properties compared to other nanoclusters. In order to study the polarization of AuMg$_9$, more intuitively, the unit sphere representation of its polarization tensor is plotted in Figure 6C. One can find the anisotropic polarization of AuMg$_9$, more specifically, the small polarization rate in the $x$-$y$ plane and the maximum polarization rate in the $z$-direction (i.e., the direction of the line connecting the leftmost Au and the rightmost Mg in the figure).

Figure 6B exhibits the static hyperpolarizability $\beta(\infty)$ of the AuMg$_n$ nanoclusters and their projection values in the dipole moment direction $\beta_{\text{prj}}(\infty)$. Since $\beta_{\text{prj}}(\infty)$ can be measured by the electric field-induced second harmonic generation experiment (EFISH), it serves as a guide for experiments. Specifically, $\beta$ increases from AuMg$_2$ to a maximum value of AuMg$_5$, then gradually decreases to a minimum value of AuMg$_9$, and increases again afterward. Interestingly, the $\beta$ and $\beta_{\text{prj}}$ of AuMg$_9$ and the nanoclusters smaller than it are exactly equal, indicating that its $\beta$ is isotropic with the dipole moment. However, starting from AuMg$_{10}$ nanocluster, the two curves are reversed, forming a mirror-symmetric trend. Figure 6D shows the unit sphere representation of static
FIGURE 5 | The ELF analysis for Mg-Mg and Au-Mg chemical bonds for AuMgn (n = 3, 4, 9, 10) nanoclusters.

FIGURE 6 | (A) Static polarizabilities \(\alpha(\omega)\), (B) Static hyperpolarizabilities \(\beta(\omega)\) for the ground state of AuMgn (n = 2–12) nanoclusters, (C) The unit sphere representation of static polarizability tensor \(\alpha\), (D) The unit sphere representation of static hyperpolarizability tensor \(\beta\) of AuMgn nanocluster.
hyperpolarizability tensor $\beta$ of AuMg$_9$, it is found that $\beta$ is also anisotropic, with a maximum in the z-direction, and changes in the x-y plane as the Mg atoms surround it. In conclusion, relative to other nanoclusters, AuMg$_9$ exhibits distinctive nonlinear optical properties.

**Boltzmann Distribution Weighted Average Spectra of IR and Raman**

For the ground state AuMg$_n$ nanoclusters, the infrared and Raman spectra with weighted average of the Boltzmann distribution were calculated for guidance experiments. The
motivation for considering the Boltzmann distribution is due to the difficulty of observing only the ground state nanoclusters in experiments, especially in the gas-phase nanoclusters. Figure 7 display the IR and Raman spectra of the weighted average of the Boltzmann distribution at room temperature. The Boltzmann distribution probabilities of each isomer at different temperatures were also calculated by the relevant equations in the Supplementary Material. The small 3D plots in each map are the corresponding weighted average spectra at 100 k, 300 k and 1000 k temperatures. As shown in Figures 7–9, the strongest absorption peaks of IR spectra are distributed in the 40–350 cm⁻¹ frequency band, while the strongest peaks of Raman spectra are
distributed in a narrower band of 20–220 cm\(^{-1}\). However, the most intense peaks of both IR and Raman weighted average spectra appear around 200 cm\(^{-1}\) as the size increases. In addition, as can be seen from the small 3D plots in each figure and Supplementary Figure S2 in the Supplementary Material, the location of the most intense peak of the weighted average spectrum does not shift as the temperature increases, but the intensity changes.

Specifically, for the weighted average IR spectra at room temperature, the nanoclusters of AuMg\(_n\) (\(n = 4–12\)) are easily distinguished as separate strong bands in the 200 cm\(^{-1}\) regions of the spectra, except for the AuMg\(_2\) and AuMg\(_3\) nanoclusters.
result is in good agreement with the results of infrared spectroscopy of pure Mg nanoclusters studied by Belyaev et al. (Belyaev et al., 2016). For the Raman weighted average spectrum at room temperature, although the strongest Raman activity peaks of AuMg₄, AuMg₅ and AuMg₆ nanoclusters appear in the low-frequency band (20–50 cm⁻¹), they still have many strong peaks in the 200 cm⁻¹ regions. Therefore, for all the Raman spectra of the AuMgₙ (n = 2–12) nanoclusters, the 200 cm⁻¹ regions can be more easily distinguished as individual strong bands. In conclusion, it was computationally shown that the formation of AuMgₙ (n = 2–12) nanoclusters at room temperature is possible to identify these nanoclusters by IR and Raman spectroscopy.

The Average Bond Distance and Average Nearest Neighbor Distance

In order to provide more data support for future possible experiments, the average bond distance and average nearest neighbor distance were calculated. As shown in Figure 10, the average nearest neighbor distance and bond distance for Au-Mg and Mg-Mg in the ground state of AuMgₙ (n = 2–12) clusters display some interesting conclusions. Figures 10A,B show that, overall, the nearest neighbor distance for Au-Mg becomes larger as the cluster size increases (except for n = 8 and 12), while Mg-Mg is overall decreasing. The average nearest neighbor distance of Au-Mg is 2.68 Å, and that of Mg-Mg is 3.44 Å. Figure 10C gives the average bond distance of Au-Mg with cluster size dependence similar to the nearest neighbor distance of Au-Mg, i.e., increasing overall. However, Figure 10D demonstrates that the average Mg-Mg bond distance decreases and then increases with cluster size. Another interesting conclusion is that the local turning points of the average bond and nearest-neighbor distances for Mg-Mg and the average bond distance curves for Au-Mg occur at AuMg₉, suggesting that they influence the local stability of the clusters.

CONCLUSION

In this work, the structure of Au-doped Mgₙ (n = 2–12) nanoclusters was investigated by CALYPSO crystal search software. It is shown that the geometric growth mechanism of this nanocluster has similarities to other atom-doped Mgn clusters but also has unique features, such as the planar structure of AuMg₃ and the high symmetry cage-like structure of AuMg₉. Stability calculations show that AuMg₄ and AuMg₁₀ have high local stability, while AuMg₉ nanoclusters are the second most stable nanoclusters. The charge transfer study reveals that Au atoms are electron receivers and Mg atoms are electron donors in AuMgₙ nanoclusters. ELF analysis showed that Mg-Mg formed a covalent chemical bond while Au-Mg was an ionic bond, and the critical size for the appearance of the Mg-Mg covalent bond was found to be AuMg₉. The nonlinear optical properties of AuMgₙ nanoclusters were probed by calculating the static polarizability and hyperpolarizability, and the results indicate that AuMg₉ is a special one of interest. Boltzmann distribution weighted average IR and Raman spectroscopy studies at room temperature confirm that these nanoclusters can be identified by spectroscopic experiments. Finally, the average bond distance and average nearest neighbor distance were fully investigated.
DATA AVAILABILITY STATEMENT
The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS
B-CZ: Software, Investigation, Writing Original draft preparation. P-JD: Methodology, Investigation, Data curation, Visualization. JG: Data curation, Visualization. W-BK: Conceptualization, Methodology, Formal analysis, Investigation, Writing review and editing.

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