Structures, stabilities and infrared spectra of Ag_nCr clusters (n=2-12) by density functional theory calculation

Ngo Thi Lan[1,2,3,4], Nguyen Thi Mai[1,2], Bui Son Tung[2], Nguyen Van Dang[3,4],
and Nguyen Thanh Tung[1,2*]

[1]Graduate University of Science and Technology, Vietnam Academy of Science and Technology;
[2]Institute of Materials Science, Vietnam Academy of Science and Technology;
[3]Faculty of Physics and Technology, TNU- University of Science;
[4]Institute of Science and Technology, TNU - University of Science.
[*]Corresponding author: tungnt@ims.vast.ac.vn.

Received 29 May 2021; Revised 30 August 2021; Accepted 14 February 2022.
DOI: https://doi.org/10.54939/1859-1043.j.mst.77.2022.73-78

ABSTRACT

Nanoclusters have been emerging as potential building blocks for advanced nanostructured materials with desired catalytic, magnetic, and electronic properties. However, determining the structure of doped atomic clusters encounters many difficulties. A powerful approach to assign the ground state geometries of atomic clusters has been the comparison the recorded vibrational infrared spectra with the corresponding computed ones. In this work, we theoretically investigate the vibrational infrared spectra of the ground-state structures of Ag_nCr *(n=2-12) clusters using density functional theory (DFT) calculations. The results of the investigation are useful for in-depth studies on size growth as well as experiments for determining the cluster structures in the future.*

Keywords: Silver cluster doped chromium; Density functional theory; Infrared spectroscopy.

1. INTRODUCTION

In the past decades, silver clusters have attracted great attention because of their huge potential in optical and catalytic applications [1-3]. Silver is known as a typical metal element. While each single Ag atom has only one delocalized electron [Kr] $4d^{10}5s^1$, transition metal atoms are magnetic owing to their non-fully filled *d* orbitals. Theoretical and experimental studies have indicated that the structural geometries, physical and chemical properties of the silver host clusters can be drastically changed when adding a transition metal atom [4-6]. The cluster structure has been shown to be determined by gas-phase experiments [7]. The most effective approach to obtain the cluster geometrical information is to use the vibrational infrared spectroscopy, and structures of specific cluster size could be assigned by comparing their calculated vibrational spectra and experimental ones [8-10].

In experiments on Ag_nM^+ clusters in 2005, E. Janssens and co-workers found the quenching of the Ag_nCo^+ cluster's magnetic moment at a specific size n = 10 [4]. The size-dependent electronic, structural and magnetic properties of Ag_nFe ($n \leq 15$) clusters were also investigated by using density functional theory (DFT) [11]. This work showed that the $Ag_{10}Fe$ cluster has a cage-like structure in which the Fe atom locates at the centre of the cage. Moreover, the total magnetic moment of $Ag_{10}Fe$ is completely quenched. The quenching properties in both cases can be explained by the 18-electron counting rule of delocalized valence electrons [12]. The cationic and neutral silver clusters doped vanadium atom were also investigated, and the results of the geometrical structure show that the dopant atom V in the ground state structure favors the most highly coordinated location and the total magnetic moment of the Ag_nV^+ and Ag_nV clusters mostly comes from V atom [13, 14]. Nevertheless, none of the above-mentioned studies reported the vibrational infrared spectra of doped silver clusters as structural fingerprints for future experiments. In order to bridge this gap, we investigate the vibrational infrared spectra of the most stable structures of Ag_nCr (n=2-12) clusters using the density functional theory (DFT). It is believed that this work can provide a useful reference for understanding the relationship between the vibrational infrared spectra and the ground-state of structures, as well as give powerful guidelines for future related experimental studies.

2. COMPUTATIONAL DETAILS

The optimization geometries and electronic configurations of Ag_nCr (n=2-12) have been carried out by density theory (DFT) calculations implemented in the Gaussian 09 package [15, 16]. In this work, we used the BP86 functional with the basis sets cc-pvTZ-pp for Ag atom and cc-pvTZ for Cr one. The basis set cc-pVTZ-pp with effective core potential (ECP) already includes the relativistic effects that are crucial for the treatment of heavy elements such as silver. The reliability of the current computational scheme has been verified by comparison with early calculations on silver and chromium dimers. It can be seen that our results summarized in table 1 are in good agreement with experimental values [17, 18]. The optimization calculations followed by frequency calculations have been done for searching minimum structures of the clusters. The optimization calculations have been performed in the following ways: we first optimize the geometrically stable $Ag_{n-1}Cr$ clusters with different spin multiplicities; then one more Ag atom is added to the low-lying isomers of the previous cluster size in all plausible positions to create input structures. The geometrical structures, electronic structures, and magnetic moments of Ag_nCr global minimum clusters were explored by using the spin density. The infrared spectroscopy is determined through the optimization of the geometrical structures accompanying the frequency calculations.

Table 1. *The bond lengths (R) and dissociation energies (D_e) of ground state Cu_2 and Cr_2 dimer,* *^{a} Refs. [18], ^{b} Refs. [17], ^{c} Ref. [19], ^{d} Ref. [20].*

Dimer	Functional/Basis set	R (A^0)		D_e (eV)	
		Calc.	Expt.	Calc.	Expt.
Ag_2	BP86/cc-pvTZ-pp	2.56	2.53 ^{a}	1.62	1.63 ± 0.03 ^{a}
	BP86/LanL2DZ	2.48		1.60	
	B3LYP/LanL2DZ	2.45		1.58	
Cr_2	BP86/cc-pvTZ	1.68	1.68^b	1.55	1.56 ± 0.3$^{a, c}$
AgCr	BP86/cc-pvTZ-pp	2.55	2.56^d	1.45	1.40^d
	BP86/LanL2DZ	2.59		1.44	
	B3LYP/LanL2DZ	2.63		1.32	

3. RESULTS AND DISCUSSION

3.1. The growth mechanism

The growth mechanism of Ag_nCr (n=2-12) clusters conform to a clear law. As illustrated in figure 1, the trapezoid (n=2-4) and icosahedron (n=5-12) structures are two fundamental frameworks for the growth process of Ag_nCr (n=2-12) clusters. The lowest-lying $Ag_{n+1}Cr$ cluster is formed by one Ag adatom on the ground state of the Ag_nCr cluster. The ground state structure of Ag_nCr cluster prefers plane structure at small size (n=2-5). The two- to three-dimensional structural transition for Ag_nCr cluster occurs at n=5. For the 3D clusters, the number of isomers increases rapidly with increasing the size of clusters. The optimized structures indicate that the relative energies of $CrAg_n$ clusters at the same size increase inversely with the decrease in the coordination number of the Cr atom. The results obtained with different $CrAg_n$ isomers show that the Cr atom tends to occupy the most highly coordinated position and is gradually encapsulated in the center by the Ag atoms which are predicted as the most stable structures. This may be attributed to the principle of maximum overlap in the chemical bond theory of complexes. The icosahedron $Ag_{12}Cr$, in which the Cr atom is located at the central position of the Ag_{12} cage, is found to be stable in the singlet spin state.

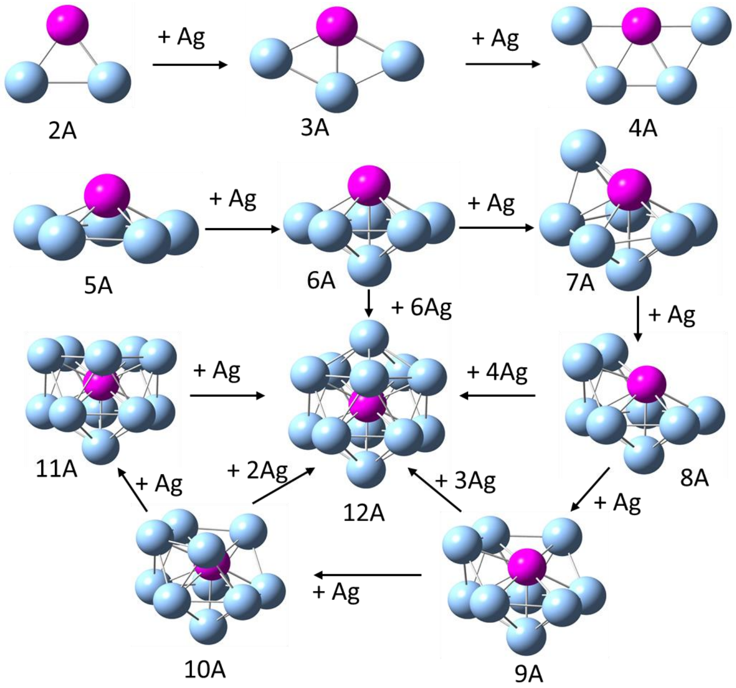

Figure 1. *The growth diagram of the Ag_nCr (n=2-12) clusters.*

3.2. Relative stabilities

In order to examine the influence of the Cr atom on the thermodynamic stabilities of Ag_nCr (n=2-12) clusters, we calculated their dissociation energies (DE in eV). In our work, we conduct a calculation of the fragmentation of Ag_nCr clusters in two major possible channels: dissociating either a Cr or an Ag atom. The calculated dissociation energies are determined by using the following formulas:

$$DE(Cr) = E(Ag_n) + E(Cr) - E(CrAg_n) \quad (1)$$

$$DE(Ag) = E(CrAg_{n-1}) + E(Ag) - E(CrAg_n) \quad (2)$$

where E represents the energy of the corresponding cluster or atom. The DEs (eV) of Ag_nCr (n=2-12) clusters for the two dissociation channels, which are defined as the different between the total electronic energies of the species formed in each dissociation channel and the electronic energies of the parent clusters, are also shown in figure 2. The results indicate that for small cluster sizes Ag_nCr (n=2-8) the energy required to lose a Cr or an Ag atom is quite similar. The Ag_2Cr cluster is the most unstable cluster since it requires only 0.62 eV to dissociate into a Cr atom and Ag_2 cluster. The larger cluster sizes (n=9-12) show the opposite picture. While the loss of an Ag atom to form $Ag_{n-1}Cr$ is the most energetically preferred dissociation channel, the other channel to decay a Cr atom requires higher energies. The calculated DEs indicates that Ag_9Cr is the most stable species among the doped silver ones, and even more stable than the icosahedral $Ag_{12}Cr$ structure. For the Ag_9Cr cluster, the dissociation energies in both channels are pretty high. The minimum energy to fragment into an Ag atom and Ag_8Cr cluster is 2.58 eV. This value is even higher than that of icosahedral $Ag_{12}Cr$ clusters (2.30 eV). Therefore, the Ag_9Cr and $Ag_{12}Cr$ clusters are considered as super atomic.

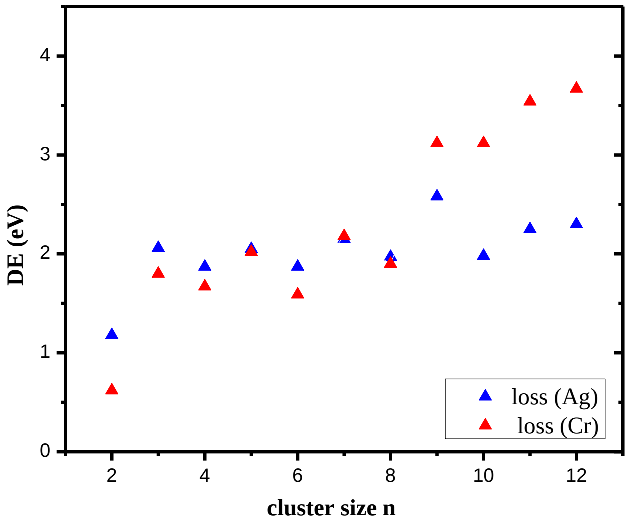

Figure 2. *The dissociation energies of the ground state structures of Ag_nCr (n=2-12) clusters: The small blue triangles represent for loss of an Ag atom and the red ones for the loss of a Cr atom.*

3.3. Infrared Spectroscopy

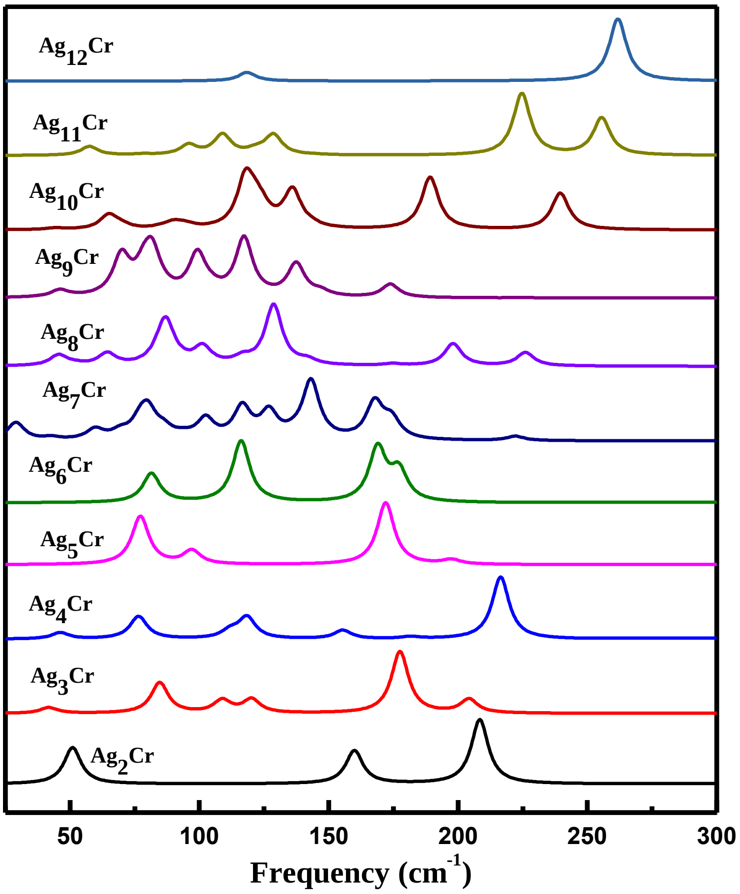

Figure 3. *The IR spectra of Ag_nCr (n=2-12) clusters.*

Figure 3 displays the IR spectra of Ag_nCr (n=2-12) clusters. Most of the spectral peaks we observed are in the frequency range from 0 cm^{-1} to 250 cm^{-1}. The IR of Ag_nCr (n=2-12) clusters show that the peaks at higher frequencies (more than 150 cm^{-1}) correspond to the vibrational mode of the Ag-Cr bonds. The Ag-Ag vibrational modes are assigned for lower frequency peaks. The spectrum of Ag_9Cr cluster is contributed from all eight modes, in which the peaks at ~ 82 cm^{-1} and ~ 174 cm^{-1} are assigned for the vibrational mode of Ag-Cr in the Ag_9 frame. Three other small peaks centered at ~ 99 cm^{-1} and 117 cm^{-1} correspond to the symmetrical vibrational mode of the Ag-Ag bonds. Unlike the Ag_9Cr cluster, the IR spectra of $Ag_{12}Cr$ appear only a high peak at high frequency ~ 262 cm^{-1} corresponding to the vibrational mode of high-symmetry Ag-Cr bonds.

4. CONCLUSION

The density functional theory (DFT) method using BP86 functional in conjunction with the basis set cc-pVTZ-pp for Ag and cc-pvTZ for Cr level has been performed to study the structures, stabilities and importantly search for the possible infrared vibrational spectra of Ag_nCr (n=2-12), which have not been available in literature yet. We hope that our findings will be useful for the theoretical understanding of doped Ag_nCr clusters as well as for aiding experiments to determine the structures of Ag_nCr species.

Acknowledgment: *This research was financially supported by the Vietnam Ministry of Education and Training under grant number B2020-TNA-16 and the Institute of Materials Science, Vietnam Academy of Science and Technology under grant CS.13/20-21.*

REFERENCES

[1]. Bertha Molina, A.T.-F, "*Thiolated Au18 cluster: preferred Ag sites for doping, structures, and optical and chiroptical properties"*, Physical Chemistry Chemical Physics, 18, 1397-403, (2016).

[2]. Chaoling Du, B.W., Fan Sun, Mingli Huang, ChongJun He, YouWen Liu, XueJin Zhang, DaningShi, "*Refractive index sensitivities of plane Ag nanosphere cluster sensors*", Sensors and Actuators B: Chemical, 215, 142-5, (2015).

[3]. Lynn A. Peyser, A.E.V., Andrew P. Bartko, Robert M. Dickson, "*Photoactivated Fluorescence from Individual Silver Nanoclusters*", Science, 291, 103-6, (2001).

[4]. E. Janssens, S.N., X. Wang, N. Veldeman, R.E. Silverans, and P. Lievens, "*Stability patterns of transition metal doped silver clusters: Dopant- and size-dependent electron delocalization*", The European Physical Journal D, 34, 23-7, (2005).

[5]. Nguyen Thi Mai, Ngo Thi Lan, Ngo Tuan Cuong, Nguyen Minh Tam, Son Tung Ngo, Thu Thi Phung, Nguyen Van Dang, Nguyen Thanh Tung, "*Systematic Investigation of the Structure, Stability, and Spin Magnetic Moment of* CrM_n *Clusters (M = Cu, Ag, Au, and n = 2−20) by DFT Calculations*", ACS Omega, 6, 20341−20350, (2021).

[6]. P.L. Rodriguez-Kesler, A.R. Rodriguez-Dominguez, "*Structural, electronic, and magnetic properties of* Ag_nCo *(**n** = 1–9) clusters: A first-principles study*", Computational and Theoretical Chemistry, 1066, 55-61, (2015).

[7]. Duncan M. A, "*Invited review article: laser vaporization cluster sources*", Rev. Sci. Instrum. 83, 041101, (2012).

[8]. Yejun Li, Jonathan T. Lyon, Alex P. Woodham, Andr Fielicke, and Ewald Janssens, "*The Geometric Structure of Silver-Doped Silicon Clusters*", Chem Phys Chem, 15, 328 – 336, (2014).

[9]. Lester Andrews and Angelo Citra, "*Infrared Spectra and Density Functional Theory Calculations on Transition Metal Nitrosyls. Vibrational Frequencies of Unsaturated Transition Metal Nitrosyls*", *Chem. Rev*, 102, 885–912, (2002).

[10]. Peter L. Rodríguez-Kessler, Adán R. Rodríguez-Domínguez, Desmond MacLeod Carey, and Alvaro Muñoz-Castro, "*Structural characterization, reactivity, and vibrational properties of silver clusters: A new global minimum for* Ag_{16}", Phys. Chem. Chem. Phys, 22, 27255-27262 (2020).

[11]. R. Dong, X. Chen, H. Zhao, X. Wang, H. Shu, Z. Ding, L. Wei, *Structural, electronic and magnetic properties of* Ag_nFe *clusters (n ⩽ 15): local magnetic moment interacting with delocalized electrons*, J. Phys. B: At. Mol. Opt. Phys, 44, 035102, (2011).

[12]. Y. Gao, X. Liu, Z. Wang, "*Ce@*Au_{14}*: A Bimetallic Superatom Cluster with 18-Electron Rule*", J. Electronic Materials, 46, 3899–3903, (2017).

[13]. R. Xiong, D. Die, L. Xiao, Y. F. Xu, X. Y. Shen, *"Probing the Structural, Electronic, and Magnetic Properties of Ag_nV (n=1-12) clusters"*, Nanoscale Res. Lett., 12, 625, (2017).
[14]. V. M. Medel, A. C. Reber, V. Chauhan, P. Sen, A. M. Koster, P. Calaminici, S. N. Khanna, "*Nature of Valence Transition and Spin Moment in Ag_nV^+ Clusters*", J. Am. Chem. Soc, 136, 8229–8236, (2014).
[15]. Frisch, M.J., et al., *Gaussian 09*, Revision A.02, Gaussian. Inc., Wallingford. (2009).
[16]. P. Hohenberg and W. Kohn. "*Inhomogeneous Electron Gas*", Physical Review, 136, B864, (1964).
[17]. Kundig E P, M.M., Ozin G, "*Matrix synthesis and characterization of dichromium, Cr_2*", Nature, 254, 503–4, (1975).
[18]. B. Simard, P. A.Hackett, A. M. James, P. R.R.Langridge-Smith, *"The bond length of silver dimer"*, Chem. Phys. Lett., 186, 415-422, (1991).
[19]. Kant A, S.B. "*Dissociation energy of Cr_2*", Journal Chemistry Physics, 45, 3161–2, (1966).
[20]. S. F. Li, Z.S., Shuli Han, Xinlian Xue, F. Wang, Q. Sun, Yu Jia, and Z. X. Guo. "*Role of Ag-doping in small transition metal clusters from first-principles simulations*", Journal Chemistry Physics, 131, 184301, (2009).
[21]. P. J. Hay, W. R. Wadt, "*Ab Initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg*", J. Chem. Phys, 82, 299, (1985).

TÓM TẮT

Cấu trúc, độ ổn định và quang phổ hồng ngoại của cụm nguyên tử Ag_nCr (n=2-12): một nghiên cứu lý thuyết

Các cụm nguyên tử nhân tạo đang nổi lên như những vật liệu tiềm năng, với các đặc tính quang học, từ tính, xúc tác rất là tốt. Tuy nhiên, cho đến nay, việc xác định cấu trúc của các cụm nguyên tử pha tạp vẫn gặp rất nhiều khó khăn. Một trong những cách tiếp cận tốt nhất để xác định cấu trúc hình học của các cụm nguyên tử ở trạng thái cơ bản là so sánh phổ dao động hồng ngoại đo được bằng thực nghiệm với phổ được tính toán tương ứng. Trong bài báo này, chúng tôi tiến hành khảo sát về mặt lý thuyết phổ dao động hồng ngoại của các cấu trúc ở trạng thái cơ bản ứng với các cụm nguyên tử Ag_nCr (n=2-12) bằng cách sử dụng phương pháp lý thuyết phiếm hàm mật độ (DFT). Các kết quả thu được của nghiên cứu này làm tiền đề quan trọng cho các nghiên cứu chuyên sâu về sự tăng trưởng kích thước cũng như các thí nghiệm xác định cấu trúc các cụm nguyên tử trong tương lai.

Từ khóa: Cụm nguyên tử bạc pha tạp Cr; Phiếm hàm mật độ; Quang phổ hồng ngoại.