Research paper

Polarization of electrostatic charge in neutral Ag-Au alloy clusters

Eunhak Lim[a], Jiyoung Heo[b], Kit H. Bowen[c], Seong K. Kim[a],[*]

[a] *Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea*
[b] *Department of Green Chemical Engineering, Sangmyung University, Chungnam 31066, Republic of Korea*
[c] *Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA*

HIGHLIGHTS

- Pronounced polarization of electrostatic charge is found in small Ag_m, Au_n, and Ag_mAu_n clusters.
- The charge is strongly affected by the mode of interactions with neighboring atoms.
- Two simple, phenomenological rules are derived regarding the charge distribution.

ABSTRACT

In our theoretical investigation for small Ag-Au alloy clusters, we found that pronounced polarization of their electrostatic charge occurs with some generic regularities. We propose a set of "rules" for the charge distribution, which may be extended to larger Ag-Au alloy clusters or even bulk solids: (1) atoms in lower-coordinated sites tend to be charged more negatively or less positively; (2) the charge of Au is affected by nearest neighbor atoms only, contrary to the case of Ag. The origins of these phenomenological rules may include site-dependent electronic polarization and the difference in s/p hybridization between Ag and Au.

1. Introduction

Silver (Ag) and gold (Au) are representative noble metals that have been in wide-ranging use since antiquity from minting coinage to removing pathogens. They were mainly used in the bulk phase but also in the form of nanomaterials, which have become the subject of intense research in the last two decades for applications in plasmonics, spectroscopy, sensors, catalysis, and medicine [1–11]. Ag and Au together form a nearly ideal binary alloy as they are miscible over a wide range of composition and size from atomic clusters to the bulk phase.

The high miscibility of Ag and Au results from their common valence electron configuration ($d^{10}s^1$) and nearly identical lattice constants (4.086 Å for Ag and 4.072 Å for Au at 293 K) [12]. However, there exists a significant difference in homonuclear bond energies between the two elements (1.65 eV for Ag-Ag vs. 2.29 eV for Au-Au) [13], which would have hindered full atomic mixing, were it not for the large heteronuclear bond energy for Ag-Au (2.06 eV) [13]. The latter is greater than the average of the two homonuclear bond energies and only slightly smaller than the Au-Au bond energy, which leads to the high thermodynamic stability of the Ag-Au alloy even when Ag and Au atoms assume nearly random atomic arrangements in the alloy.

On the other hand, the electrophilic trend of these two elements is so considerably different (electron affinity of Ag and Au being 1.30 and

2.31 eV; electronegativity of Ag and Au being 1.93 and 2.54, respectively) that the electrostatic charge distribution may present a non-uniform, complex landscape in the atomic scale on the surface of an Ag-Au alloy even though the alloy itself may have a well-dispersed atomic arrangement.

There have been many studies on the geometrical and electronic structures of the Ag-Au alloy clusters [14–21], including some work of particular relevance to their electrostatic charge [20,21], but little is known about the generic feature of the electrostatic charge distribution in these clusters and the principle that governs it. In this study, we carried out density functional theory calculations for various Ag-Au alloy clusters and found a great degree of polarization of electrostatic charge in the Ag-Au alloy clusters. We also found some generic regularities in their electrostatic charge distribution, which appear clearly evident even from the limited range of cluster size we studied. We came to propose a set of rules for it, which may even predict a rudimentary charge distribution in larger Ag-Au clusters or bulk solids.

2. Theoretical methods

We carried out density functional theory calculations using Gaussian 09 package (Revision D.01) [22] with the conventional B3LYP [23] exchange-correlation functional. All calculations were performed
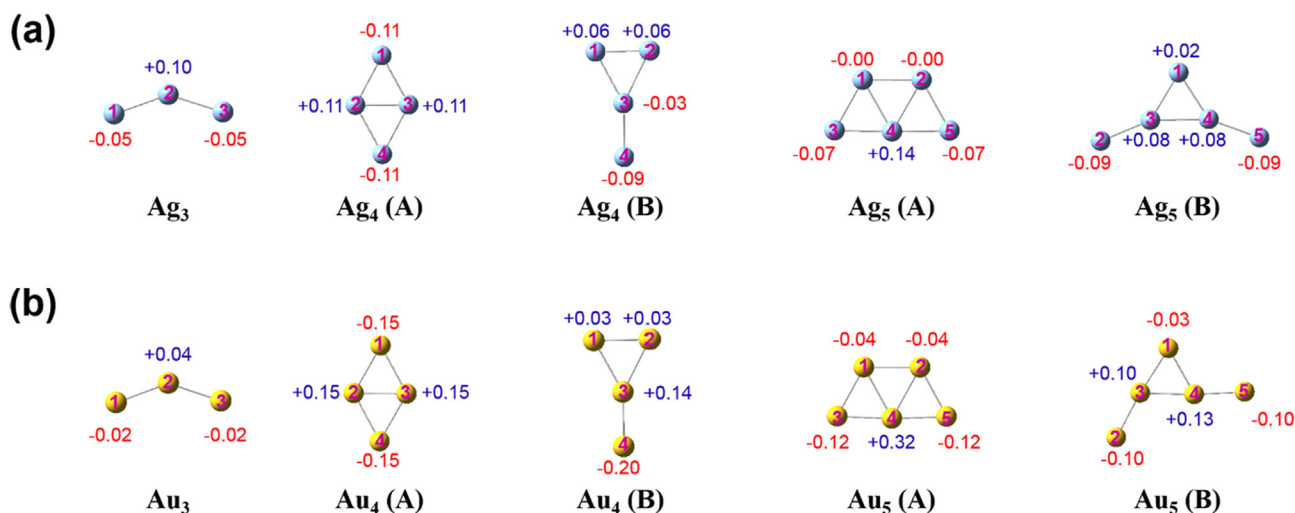
Fig. 1. Optimized geometries of neutral (a) Ag_n ($n = 3, 4, 5$) and (b) Au_n ($n = 3, 4, 5$) clusters. Atomic charges obtained by Mulliken population analysis are shown in blue (positive charge) or red (negative charge), while the atomic position in the given cluster is marked in magenta on each atom.

without symmetry constraints. The LANL2DZ [24–26] basis set with effective core potential was used for silver and gold. All local minimum geometries were verified to be a stationary state by frequency analysis. Atomic charges were obtained by Mulliken population analysis.

3. Results and discussion

Before investigating the Ag-Au binary alloy clusters, we first examined the pure Ag_n and Au_n clusters ($n = 3, 4,$ and 5; Fig. 1). From their geometries and atomic charge distributions, we note that the electronic charge tends to be concentrated on the pointed ("outer") atoms with fewer chemical bonds, leaving the other ("inner") atoms with a positive charge since all clusters are electrostatically neutral as a whole. For example, atoms 1 and 3 of Ag_3 and Au_3 with only 1 chemical bond are negatively charged while the central atom 2 with 2 chemical bonds is positively charged. In the case of tetramers, atoms 1 and 4 of Ag_4 (A) and Au_4 (A) are the sites of negative charge as they form only 2 chemical bonds, whereas atoms 2 and 3 with 3 bonds take up the counter positive charge. Likewise, atom 4 of Ag_4 (B) and Au_4 (B) with only 1 chemical bond assumes a predominant negative charge. (The negative charge on the 3-coordinated atom 3 of Ag_4 (B) seems an interesting anomaly.) For pentamers, atom 4 of Ag_5 (A) and Au_5 (A) has a large positive charge since it forms the maximal 4 chemical bonds while the counter negative charge is mainly piled up on atoms 3 and 5 with 2 bonds rather than atoms 1 and 2 with 3 bonds. The above regularity that we now call our "Rule 1" may be invoked to make sense of the charge distribution in other clusters, such as the negative charge on atoms 2 and 5 along with a corresponding positive charge on atoms 3 and 4 of Ag_5 (B) and Au_5 (B). Hence, we draw a tentative conclusion that our Rule 1 is consistent with a generic feature of the electrostatic charge distributions commonly found in pure Ag and Au clusters.

Next, we generated a full library of neutral Ag-Au binary alloy clusters for up to 5-atom species with different elemental compositions and structures (Fig. 2). In almost all clusters, Ag atoms are positively charged while Au atoms assume a negative charge, as dictated by the aforementioned disparity in the electron affinity and electronegativity of these elements. We also verify that our Rule 1 derived from pure Ag and Au clusters applies even to the Ag-Au alloy clusters. For instance, in the 4A family (Fig. 2(c)), atoms in the outer, lower-coordinated positions are more negatively charged (as with Au atoms 1 and 4 against Au atom 3 in 4A-1, Au atom 4 against Au atom 3 in 4A-2, Ag atom 1 against Ag atoms 2 and 3 in 4A-4) or less positively charged (as with Ag atom 1 against Ag atom 2 in 4A-2). Such a site dependence of charge is representatively apparent in 5A-4, where atom 4 has a rather large

positive charge ($+0.18$) even though it is the same gold atom as atoms 3 and 5, since it is located at the innermost position and thus forms 4 chemical bonds with all other atoms.

Further examination of atomic Mulliken charges in Fig. 2 reveals another regularity that we came to call "Rule 2": the atomic charge of Au is mostly determined by the nearest neighbour atoms only, whereas the atomic charge of Ag is considerably affected by atoms farther away. In other words, the charge of a gold atom does not change greatly when its next nearest neighbour atoms indirectly bonded to it are replaced by the other element, but the charge of a silver atom is rather strongly affected by such a substitution. For example, as 5A-6, 5A-13, 5A-15, and 5A-17 share the same arrangement of atoms 1, 3, and 4, their different elemental compositions for atoms 2 and 5 indirectly bonded to atom 3 little affect the charge on the Au atom 3 (between -0.45 and -0.47).

In contrast to Au, the charge on Ag is considerably affected when atoms beyond the nearest neighbour sites are substituted. For example, 5A-2, 5A-7, 5A-9, and 5A-12 share the same arrangement of atoms 1, 3, and 4 but the positive charge on the Ag atom 3 changes significantly (between $+0.23$ and $+0.46$) as the atoms 2 and 5 change their compositions. The most striking case of Rule 2 is observed in the 5B family, where the positive charge on the Ag atom 1 of 5B-1 and 5B-2 is strongly dependent on the elemental composition of atoms 2 and 5, whereas the negative charge on the Au atom 1 of 5B-3 and 5B-4 is little affected by them. After all, the complete removal of atoms 2 and 5 from 5B-3 and 5B-4 results in only a mild increase in the charge of atom 1 (as in Ag_2Au_1). Hence, we cautiously suggest that the strong electron-withdrawing nature of Au atom is short-ranged and does not reach beyond a single-atom range.

4. Conclusions

In conclusion, we carried out density functional theory calculations for the neat and alloy clusters of Ag and Au. Even in neat clusters, significant polarization of electrostatic charge was observed since atoms at different locations can have different coordination numbers. Polarization of electrostatic charge was more pronounced in alloy clusters since it is governed by the coordination number as well as the elemental identity of atoms. We found two distinctly generic regularities in the electrostatic charge distribution of these clusters, which were clearly apparent starting with 2- or 3-atom clusters and applicable to clusters of at least up to 5 atoms. They were summarized in two rules, the first of which dictates that atoms located at the pointed ("outer") site with a smaller coordination number tend to be charged more
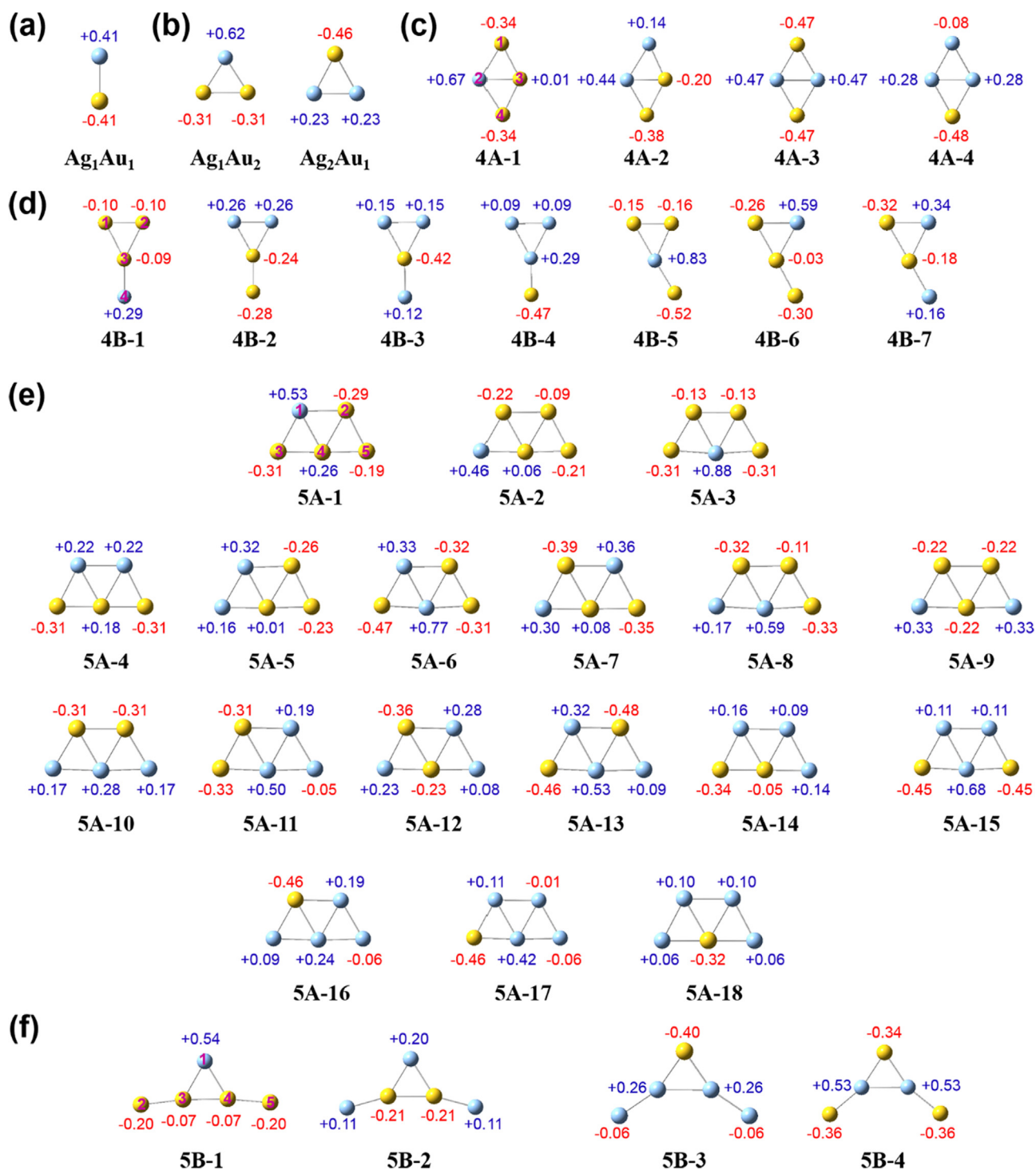
Fig. 2. Optimized geometries of neutral (a) Ag_1Au_1, (b) Ag_nAu_{3-n}, (c) Ag_nAu_{4-n} (4A), (d) Ag_nAu_{4-n} (4B), (e) Ag_nAu_{5-n} (5A), and (f) Ag_nAu_{5-n} (5B) binary alloy clusters. Mulliken charges are indicated in blue (positive charge) or red (negative charge), while the representative atomic positions are marked in magenta.

negatively or less positively. Our second rule states that the atomic charge of Au is mainly governed by the directly bonded neighbouring atoms but the atomic charge of Ag is affected also by atoms beyond the nearest neighbours. The origin of rule 1 may lie in the fact that, even for a given element, its atomic polarizability is different at different atomic locations. An outer-lying atom with a lower coordination number would exhibit a more spatially disperse electronic charge and higher polarizability that results in a larger "spill-over" effect of electronic charge to the periphery of the cluster. On the other hand, rule 2 may stem from a higher degree of localization of the Au 6s orbital than the

Ag 5s orbital or their different degrees of s/p hybridization. Although the origins of these two phenomenological rules are not fully understood yet, we nevertheless note that these rules provide a quick and effective guide to explain and may even predict a rudimentary charge distribution in these clusters. Further studies are underway to investigate the underlying nature of these rules and also to expand our study to other cluster systems.

Acknowledgement

This work was supported by the SGER Program (NRF-2015R1D1A1A02061817) and the Global Frontier R & D Program for Multiscale Energy System (NRF-2014M3A6A7060583) for SKK and the Basic Science Research Program (2018R1D1A1B07043430) for JH through the National Research Foundation of Korea. KHB also acknowledges the support of this work by the Air Force Office of Scientific Research (AFOSR) under grant no. FA9550-15-1-0259.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cplett.2018.08.030.

References

[1] A.M. Alkilany, S.E. Louse, C.J. Murphy, The gold standard: gold nanoparticle libraries to understand the nano-bio interface, Acc. Chem. Res. 46 (2013) 650–661.

[2] Y. Zhang, X. Cui, F. Shi, Y. Deng, Nano-gold catalysis in fine chemical synthesis, Chem. Rev. 112 (2012) 2467–2505.

[3] D.A. Giljohann, D.S. Seferos, W.L. Daniel, M.D. Massich, P.C. Patel, C.A. Mirkin, Gold nanoparticles for biology and medicine, Angew. Chem. Int. Ed. 49 (2010) 3280–3294.

[4] M. Murphy, K. Ting, X. Zhang, C. Soo, Z. Zheng, Current development of silver nanoparticles preparation, investigation, and application in the field of medicine, J. Nanomater. 2015 (2015) Article ID 696918.

[5] M. Rycenga, C.M. Cobley, J. Zeng, W. Li, C.H. Moran, Q. Zhang, D. Qin, Y. Xia, Controlling the synthesis and assembly of silver nanostructures for plasmonic applications, Chem. Rev. 111 (2011) 3669–3712.

[6] X. Tang, J. Schneider, A. Dollinger, Y. Luo, A.S. Wörz, K. Judai, S. Abbet, Y.D. Kim, G.F. Ganteför, D.H. Fairbrother, U. Heiz, K.H. Bowen, S. Proch, Very small "window of opportunity" for generating CO oxidation-active Au_n on TiO_2, Phys. Chem. Chem. Phys. 16 (2014) 6735–6742.

[7] R. Pal, L.-M. Wang, Y. Pei, L.-S. Wang, X.C. Zeng, Unraveling the mechanisms of O_2 activation by size-selected gold clusters: transition from superoxo to peroxo chemisorption, J. Am. Chem. Soc. 134 (2012) 9438–9445.

[8] R. Philip, G.R. Kumar, Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters, Phys. Rev. B 62 (2000) 13160–13166.

[9] M. Tominaga, T. Shimazoe, M. Nagashima, H. Kusuda, A. Kubo, Y. Kuwahara, I. Taniguchi, Electrocatalytic oxidation of glucose at gold-silver alloy, silver and gold nanoparticles in an alkaline solution, J. Electroanal. Chem. 590 (2006) 37–46.

[10] L. Tong, C.M. Cobley, J. Chen, Y. Xia, J.-X. Cheng, Bright three-photon luminescence from gold/silver alloyed nanostructures for bioimaging with negligible photothermal toxicity, Angew. Chem. Int. Ed. 49 (2010) 3485–3488.

[11] F.J. Ibañez, F.P. Zamborini, Chemiresistive sensing of volatile organic compounds with films of surfactant-stabilized gold and gold-silver alloy nanoparticles, ACS Nano 2 (2008) 1543–1552.

[12] I.-K. Suh, H. Ohta, Y. Waseda, High-temperature thermal expansion of six metallic elements measured by dilatation method and X-ray diffraction, J. Mater. Sci. 23 (1988) 757–760.

[13] M.D. Morse, Clusters of transition-metal atoms, Chem. Rev. 86 (1986) 1049–1109.

[14] S. Heiles, A.J. Logsdail, R. Schäfer, R.L. Johnston, Dopant-induced 2D–3D transition in small Au-coating clusters: DFT-global optimisation of 8-atom Au-Ag nanoalloys, Nanoscale 4 (2012) 1109–1115.

[15] G.F. Zhao, Z. Zeng, Geometrical and electronic structures of Au_mAg_n ($2 \le m + n \le 8$), J. Chem. Phys. 125 (2006) 014303.

[16] S. Chrétien, M.S. Gordon, H. Metiu, Density functional study of the adsorption of propene on mixed gold-silver clusters, Au_nAg_m: propensity rules for binding, J. Chem. Phys. 121 (2004) 9931–9937.

[17] L. Hong, H. Wang, J. Cheng, X. Huang, L. Sai, J. Zhao, Atomic structures and electronic properties of small Au-Ag binary clusters: effects of size and composition, J. Comput. Theor. Chem. 993 (2012) 36–44.

[18] V. Bonačić-Koutecký, J. Burda, R. Mitrić, M. Ge, G. Zampella, P. Fantucci, Density functional study of structural and electronic properties of bimetallic silver-gold clusters: comparison with pure gold and silver clusters, J. Chem. Phys. 117 (2002) 3120–3131.

[19] H.M. Lee, M. Ge, B.R. Sahu, P. Tarakeshwar, K.S. Kim, Geometrical and electronic structures of gold, silver, and gold-silver binary clusters: origins of ductility of gold and gold-silver alloy formation, J. Phys. Chem. B 107 (2003) 9994–10005.

[20] F. Chen, R.L. Johnston, Charge transfer driven surface segregation of gold atoms in 13-atom Au–Ag nanoalloys and its relevance to their structural, optical and electronic properties, Acta Mater. 56 (2008) 2374–2380.

[21] A. Shayeghi, C.J. Heard, R.L. Johnston, R. Schäfer, Optical and electronic properties of mixed Ag-Au tetramer cations, J. Chem. Phys. 140 (2014) 054312.

[22] Gaussian 09, Revision D.01, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[23] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652.

[24] 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 (1985) 270–283.

[25] W.R. Wadt, P.J. Hay, *Ab initio* effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, J. Chem. Phys. 82 (1985) 284–298.

[26] P.J. Hay, W.R. Wadt, *Ab initio* effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, J. Chem. Phys. 82 (1985) 299–310.