



## Cu, Ag and Au clusters as air pollutants hunters

Miguel Reina\*, Ana Martínez

Departamento de Materiales de Baja Dimensionalidad, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S.N. Ciudad Universitaria, P.O. Box 70-360, Coyoacán C.P. 04510, Ciudad de México, Mexico

### ARTICLE INFO

#### Article history:

Received 24 February 2018  
Received in revised form 4 March 2018  
Accepted 4 March 2018  
Available online 6 March 2018

#### Keywords:

Metal clusters  
Air pollutants  
NO<sub>2</sub> and SO<sub>2</sub> hunters  
Oxidative stress

### ABSTRACT

The reaction of small metal clusters (Cu, Ag and Au up to ten atoms and Au<sub>20</sub>) with two air pollutant (NO<sub>2</sub> and SO<sub>2</sub>) molecules is investigated. All systems under study are capable of trapping NO<sub>2</sub> and SO<sub>2</sub>, as the formation reactions are exergonic and thus thermodynamically viable. The products in the addition reactions are molecularly bonded and in most cases planar five member rings (M–O–N–O–M) are formed. Cu clusters present the most exergonic reactions followed by Ag and Au, respectively. Au clusters were used to analyze successive additions. As a result of this investigation, it is possible to conclude that Au clusters are capable of trapping up to three air pollutant (NO<sub>2</sub> and SO<sub>2</sub>) molecules. The results for Au<sub>20</sub> indicate that as the size of the cluster increases, exergonicity decreases. In summary, small metal clusters may serve as efficient materials for hunting air pollutants. Finally, this investigation may serve as an important guide for further theoretical and experimental studies, which attempt to analyze the effectiveness of small clusters to hunt air pollutants.

© 2018 Elsevier B.V. All rights reserved.

### 1. Introduction

Clusters present unique geometric shapes and very high surface-to-volume ratio; factors which influence their electronic and chemical properties. The reactivity of metal clusters has been broadly studied, providing valuable information and remarkable results [1–38]. The adsorption of small non-reactive molecules, the interaction of metal clusters with DNA and RNA bases for medical and catalysis purposes, the investigation of these systems as optoelectronic devices, and the potential applications of these systems as free radical scavenging materials are some examples of the investigations that are being carried out [29–38]. Moreover, clusters are also interesting in the context of nanodrug delivery systems [39,40].

Silver and gold represent the most outstanding clusters, due to their specific properties. They have been used as antimicrobial, antioxidant, anti-diabetic and anti-hemolytic materials [41]. In particular, several studies have focused on coinage metals (Cu, Ag and Au), as their electronic configuration with a closed *d* shell and a single *s* valence electron presents interesting chemical properties. Gold clusters are known to be more reactive with CO and O<sub>2</sub> than Cu and Ag clusters, but Cu clusters are better for scavenging free radicals than Ag and Au systems [23,24,30,31].

Copper is an integral part of many important enzymes. However, it may be released and become free to catalyze the formation of highly reactive hydroxyl radicals [42]. The anti-cancer properties of silver clusters have been demonstrated, but they also cause the production of reactive oxygen species [43]. Apparently, these are two sides of the same coin and more studies are needed to better understand the properties of clusters formed from copper and silver, as they are useful and essential, but potentially toxic to human health. The case of gold clusters is different because these appear not to be toxic [44,45]. Moreover, they provide a versatile surface chemistry that can be functionalized by ligands, to specifically interact with receptors at the surface of target cells [46,47].

In summary, copper, silver and gold clusters have attracted increasing interest due to their properties. In particular, biologically synthesized gold and silver clusters showed significantly high antioxidant activities, thus circumventing oxidative stress [41].

Oxidative stress is produced by reactive oxygen species, that are harmful to human health but these are not the only culprits. Air pollution can also be dangerous and it is well known that there is a connection between air quality and human health. The main air pollutants (for example SO<sub>2</sub> and NO<sub>2</sub>) contribute to the development of bronchitis, emphysema and asthma [48,49]. Therefore, it is very important to diminish the concentration of these molecules in order to improve air quality. The idea is that metal clusters may be very useful for this purpose.

Metal clusters are useful for scavenging free radicals and may therefore also serve as good air pollutant hunters. To analyze this

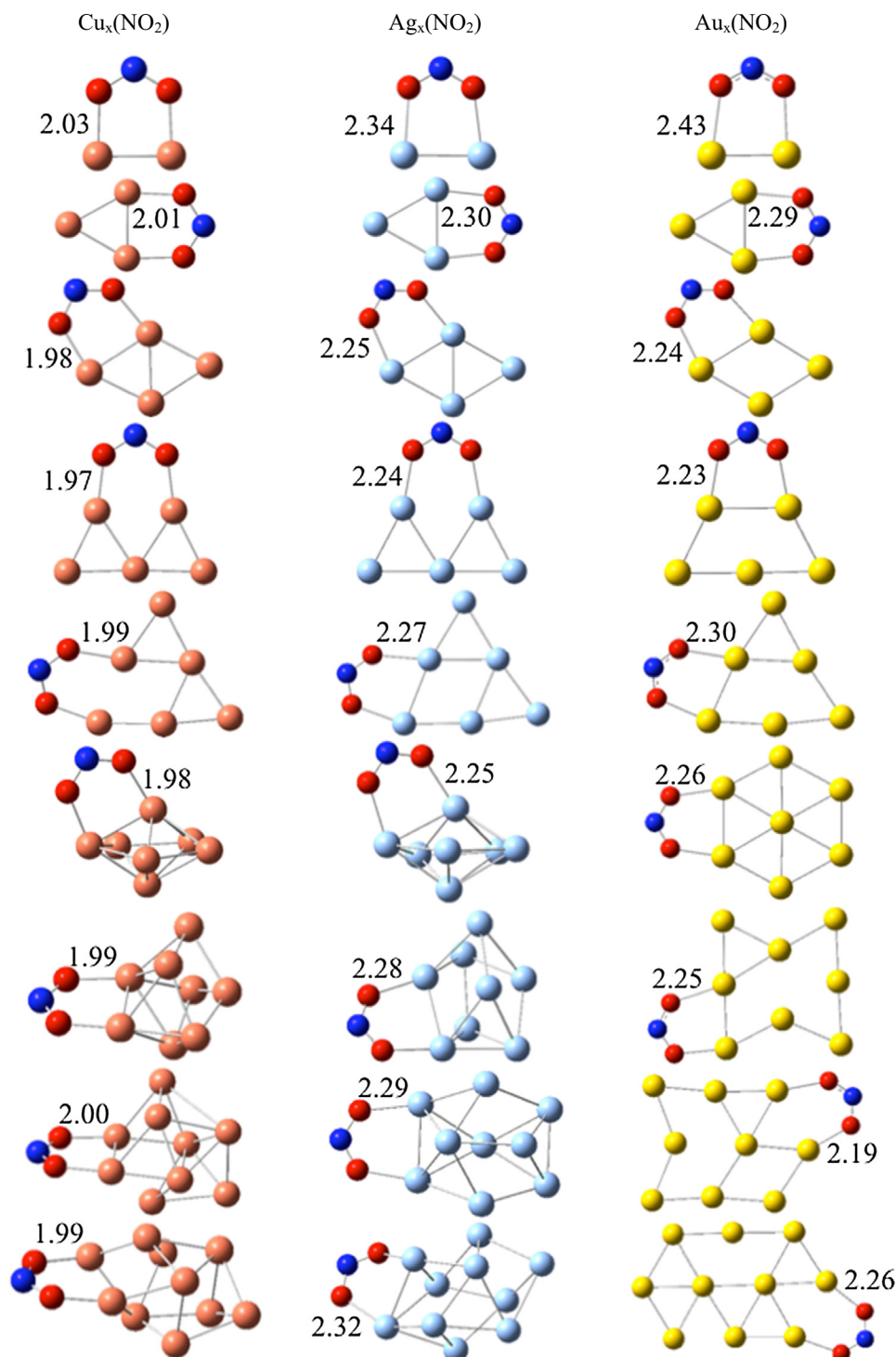
\* Corresponding author.

E-mail addresses: [mreina.2404@hotmail.com](mailto:mreina.2404@hotmail.com), [miguelreina@ciencias.unam.mx](mailto:miguelreina@ciencias.unam.mx) (M. Reina).

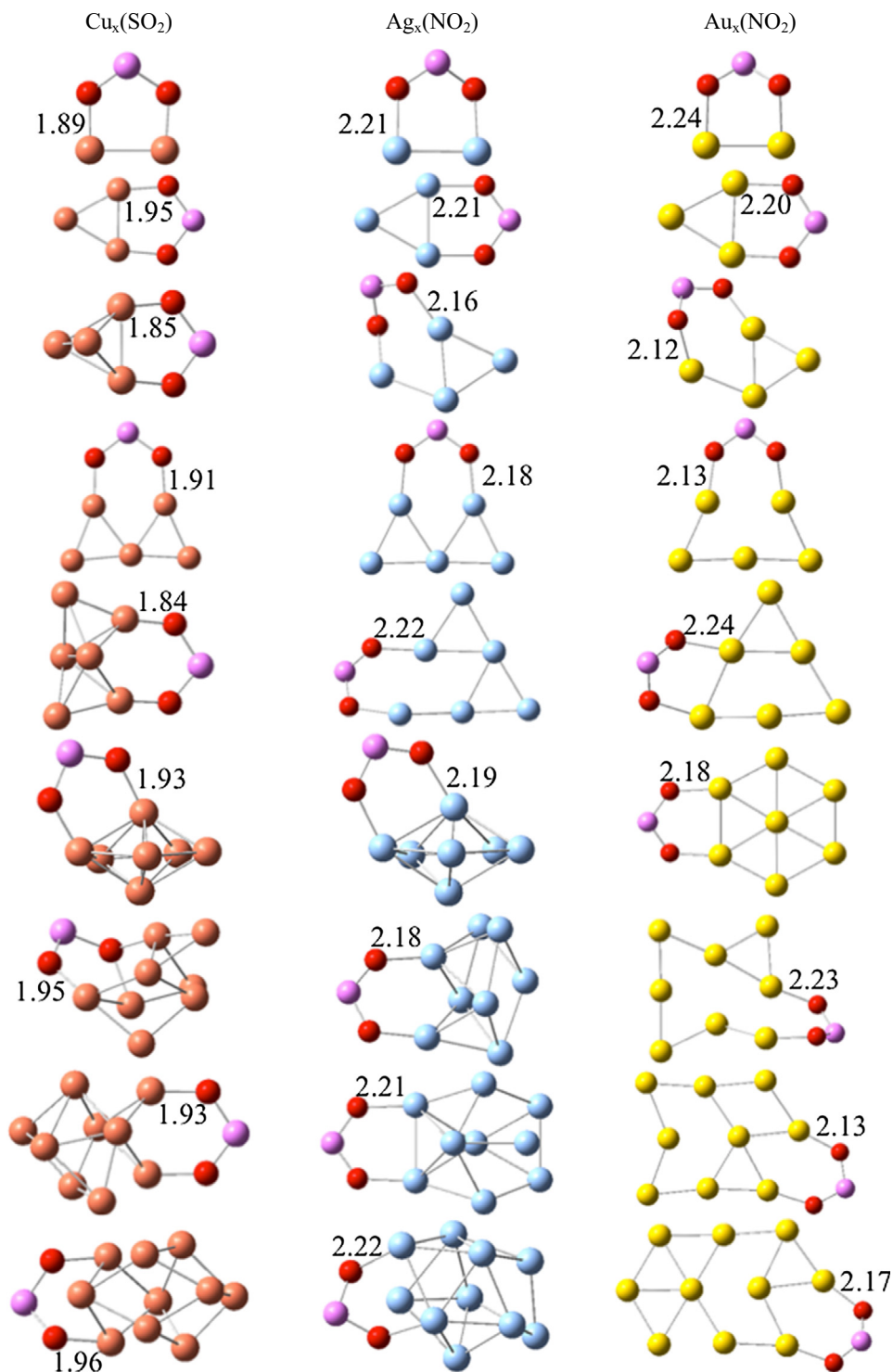
possibility, in this paper, we theoretically investigate the interaction of metal clusters with  $\text{SO}_2$  and  $\text{NO}_2$ . As will become apparent later in this work, metal clusters are able to trap these molecules. One small cluster of gold in particular, has the potential capacity to trap at least three of these molecules. These results may have important applications in the design of materials that can diminish air pollution.

## 2. Computational details

Geometry optimization and electronic calculations were performed with Gaussian 09 code [50]. Initial geometries were fully optimized at M06/LanL2DZ level of theory in gas phase [51–58]. In order to verify local minima, harmonic analyses were calculated (zero imaginary frequencies). Initial geometries for  $\text{Cu}_x$ ,  $\text{Ag}_x$  and



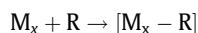
**Fig. 1.** Optimized structures of  $\text{M}_x(\text{NO}_2)$  systems ( $\text{M} = \text{Cu}$  (red),  $\text{Ag}$  (blue)  $\text{Au}$  (yellow);  $x = 2-10$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Optimized structures of  $M_x(\text{SO}_2)$  systems ( $M = \text{Cu}$  (red),  $\text{Ag}$  (blue)  $\text{Au}$  (yellow);  $\text{S}$  (purple);  $x = 2-10$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{Au}_x$  clusters ( $x = 2-10$  and  $20$ ) were described in previous reports [29,59,60]. An exhaustive search of the most stable structures was performed. To this end, several initial geometries considering all possible bond sites of the metal clusters were optimized. Planar and 3D structures were considered as well.

To investigate the atmospheric pollutant scavenger capacity of small metal clusters, Gibbs free energy values were obtained, considering the following reaction scheme:

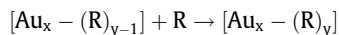


$$\Delta G = G([M_x - R]) - G(M_x) - G(R)$$

$M$  is  $\text{Cu}$ ,  $\text{Ag}$  or  $\text{Au}$ ,  $x$  corresponds to the number of metal atoms ( $2-10$ );  $R$  represents the pollutant molecules ( $\text{NO}_2$  and  $\text{SO}_2$ ); and  $[M_x - R]$  is the formed product.

We also investigated  $\text{Au}_{20}$  in order to analyze chemical properties as a function of the size of the system, and to make comparisons with previous reports [14].

To investigate the successive scavenging ability of  $\text{Au}_x$  clusters ( $x = 2-10$  and 20), successive Gibbs free energies were obtained, applying the following reaction scheme:



$$\Delta G = G([\text{Au}_x - (\text{R})_y]) - G([\text{Au}_x - (\text{R})_{y-1}]) - G(\text{R})$$

$y$  represents the number of  $\text{NO}_2$  and  $\text{SO}_2$  molecules ( $y = 1-3$ ). In all systems studied, the lowest spin multiplicity (singlet or doublet) is the most stable. For successive additions, initial geometries were the most stable systems with one less adsorbed molecule and all possible bond sites were considered.

### 3. Results and discussion

The optimized structures of  $\text{M}_x(\text{NO}_2)$  and  $\text{M}_x(\text{SO}_2)$  are presented in Figs. 1 and 2. In all structures, oxygen atoms of  $\text{NO}_2$  and  $\text{SO}_2$  interact with the metal clusters, forming a five member ring. With copper and silver, systems are planar for up to six atoms. The

exceptions are  $\text{Cu}_4\text{SO}_2$  and  $\text{Cu}_6\text{SO}_2$ , as these are three-dimensional. For gold clusters, all the optimized geometries are planar. As expected, the shortest M–O bond distance is for copper systems. Copper and silver clusters with more than six atoms adopt a three-dimensional structure. The optimized geometries are similar to the optimized structures of bare clusters previously reported. Although copper and silver clusters present three-dimensional structures, the interaction with  $\text{NO}_2$  and  $\text{SO}_2$  generates planar five member rings in most systems. Free radicals are preferably absorbed in the edges of the cluster. It can be expected similar behavior for surfaces. This could be suggesting that molecules are absorbed at edges or vacancies.

It is interesting to see that  $\text{NO}_2$  and  $\text{SO}_2$  molecules are molecularly bonded to the metal cluster. This means that molecules are trapped but not dissociated. Metal clusters in these systems do not act as catalysts. They may be scavenger (or hunters) of air pollutants. In order to do so, exergonic reactions with  $\text{NO}_2$  and  $\text{SO}_2$  are desirable. To analyze these interactions, Figs. 3 and 4 present Gibbs free energies as a function of the number of metal atoms in the clusters, for all systems being studied.

The first interesting result is that there is an odd-even alternation of  $\Delta G$  values. Systems with an odd number of metal atoms

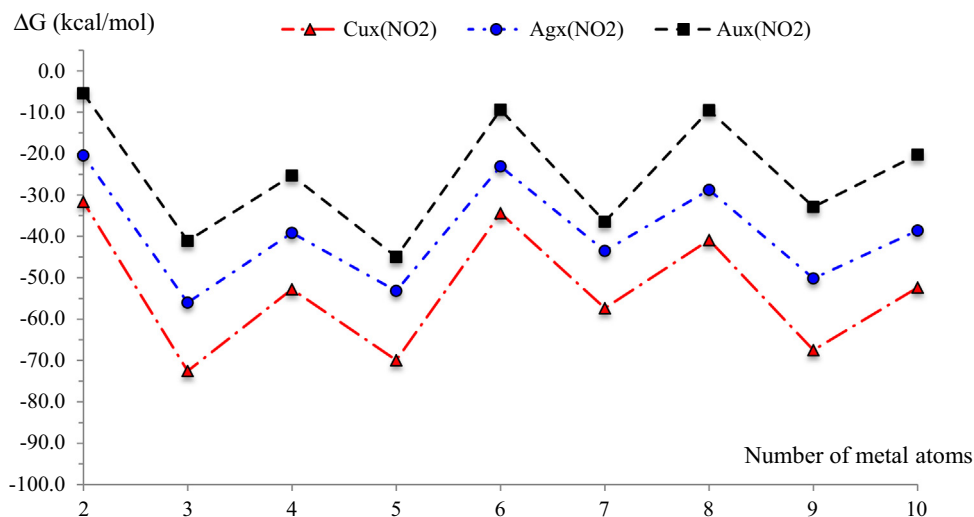


Fig. 3.  $\Delta G$  in kcal/mol for the  $\text{M}_x + \text{NO}_2 \rightarrow [\text{M}_x\text{-NO}_2]$  reaction;  $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ;  $x = 2-10$ .

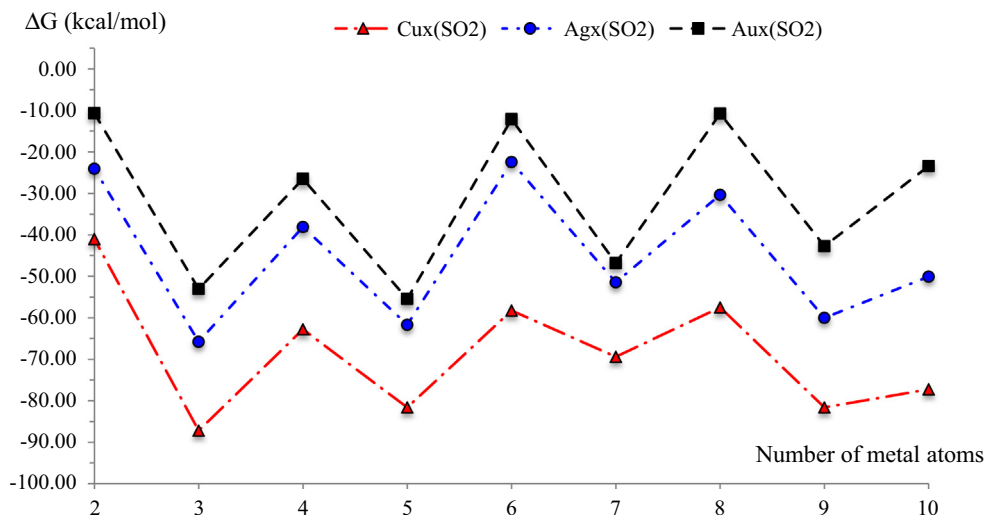


Fig. 4.  $\Delta G$  in kcal/mol for the  $\text{M}_x + \text{SO}_2 \rightarrow [\text{M}_x\text{-SO}_2]$  reaction;  $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ;  $x = 2-10$ .

(even number of total atoms) are more exergonic than those with an even number of metal atoms. The explanation for this behavior is not obvious. Thus, closed-shell systems are possibly more stable than open-shell systems, meaning that reactions that produce closed-shell systems will be more exergonic. However, this is not the case, as  $\text{NO}_2$  is a free radical, whereas  $\text{SO}_2$  is not. For  $\text{M}_x(\text{NO}_2)$ , the spin multiplicity of the systems with an odd number of metal atoms indicates that they are singlets, whereas for  $\text{M}_x(\text{SO}_2)$  they are doublets. The alternation of the  $\Delta G$  values can neither be explained by the symmetry of the structures, nor by the atomic charges. The bond of  $\text{NO}_2$  and  $\text{SO}_2$  with the metal clusters is similar in all systems. There is still no explanation for this, but the probable conclusion is that clusters with an odd-number of metal atoms

are more reactive towards these molecules than those formed from an even number of metal atoms.

The most exergonic reactions are those where copper clusters and  $\text{SO}_2$  are present. For all systems, reactions with  $\text{SO}_2$  are at least 10 kcal/mol more exergonic than reactions with  $\text{NO}_2$ . Furthermore, M–O bond distances are shorter for  $\text{SO}_2$  than for  $\text{NO}_2$ . Apparently, the bond is stronger with the first than with the second. It may be that all metal clusters react spontaneously with these two molecules, enabling them to scavenge these pollutants. Apparently, they are more effective for trapping  $\text{SO}_2$  than  $\text{NO}_2$ .

With successive additions, it is possible for more than one molecule to become bonded to the metal cluster. To investigate these successive additions, two and three molecules were attached

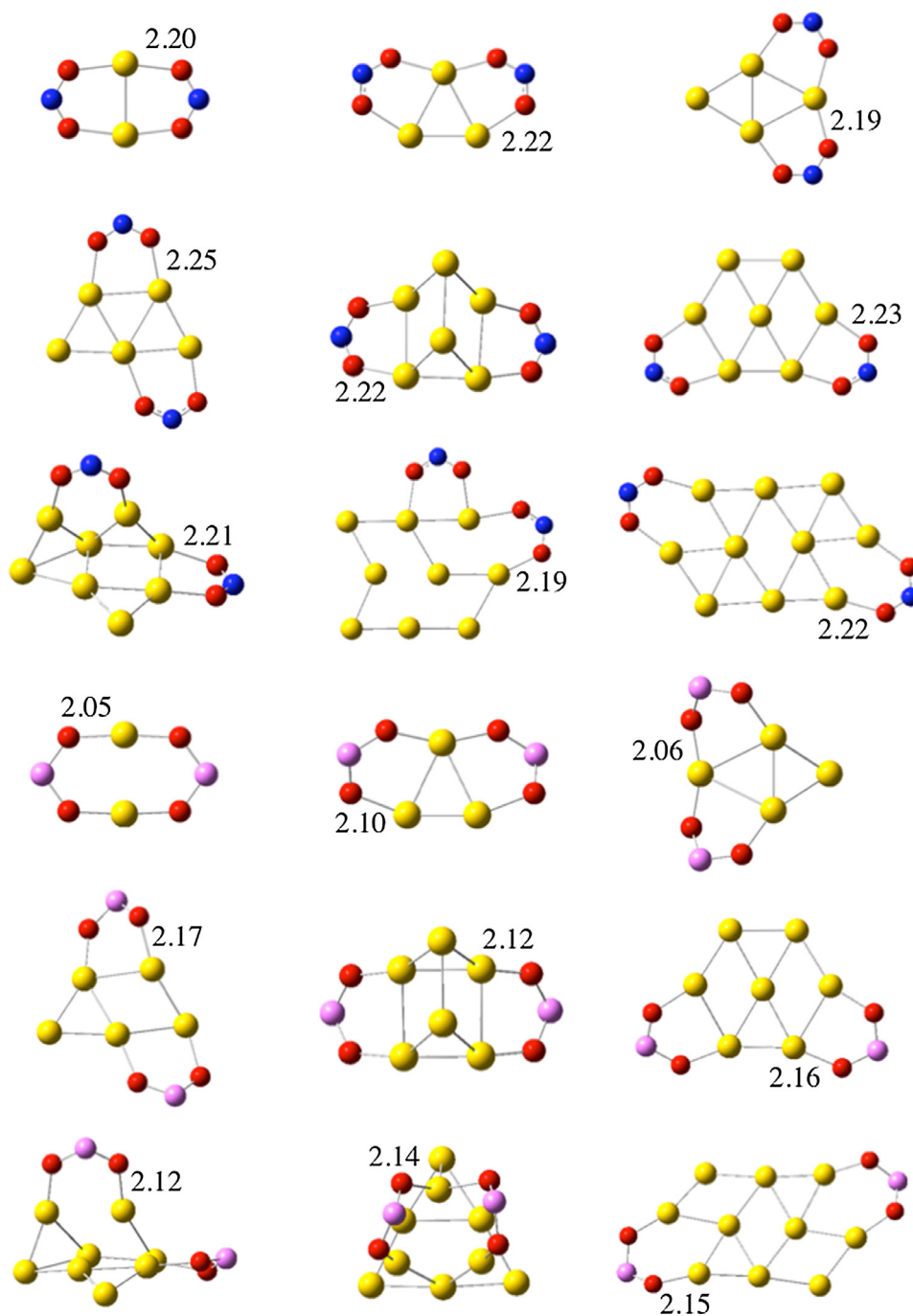


Fig. 5. Optimized structures for  $\text{Au}_x(\text{R})_2$  systems,  $x = 2-10$  and  $\text{R} = \text{NO}_2$  and  $\text{SO}_2$ .

to gold clusters. We selected gold clusters because the reactions are less exergonic than those with copper and silver. If it works with gold, it could also work with silver and copper clusters.

Figs. 5 and 6 present the most stable optimized structures of gold clusters interacting with two and three molecules of  $\text{NO}_2$  and  $\text{SO}_2$ . Several initial structures were optimized, but only the most stable geometries are included in the figures. The majority of the structures with two  $\text{NO}_2$  molecules are planar, whereas with three molecules the structures can be either planar or three-dimensional. M–O bond length is similar for all systems. Gibbs free

energies are reported in Figs. 7 and 8. These were calculated considering successive additions, i.e. a single molecule is added to any gold cluster that is already bonded to one molecule; so that a third molecule is added to any system that is already bonded to two molecules. Results are similar to those observed previously with only one molecule; once again reactions with  $\text{SO}_2$  are more exergonic than reactions with  $\text{NO}_2$ . There is also an even-odd alternation.

Analyzing the results for  $\text{Au}_2$ , interestingly, Gibbs free energy is highly exergonic on the addition of the second molecule, whereas

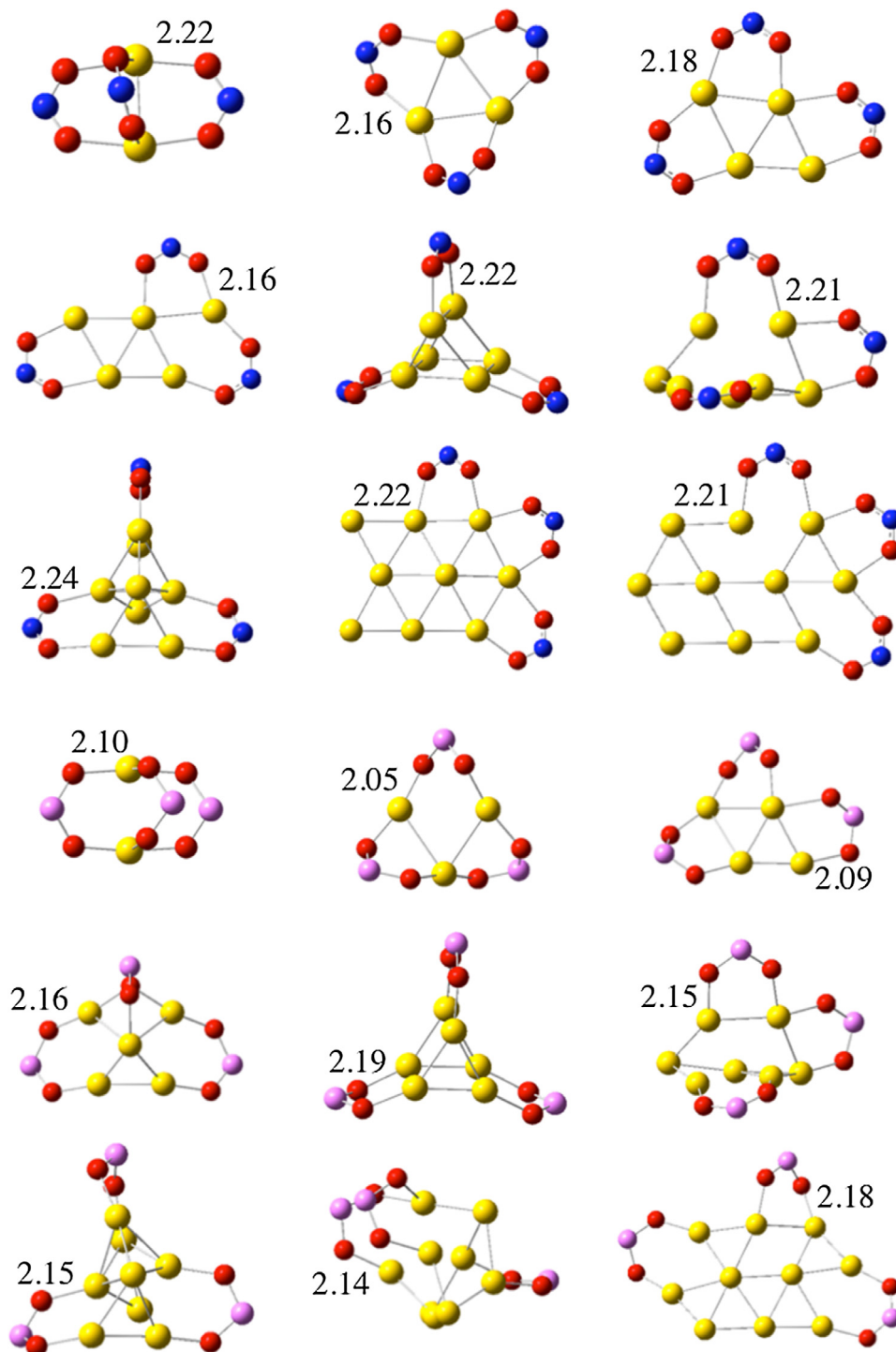


Fig. 6. Optimized structures for  $\text{Au}_x(\text{R})_3$  systems,  $x = 2-10$  and  $\text{R} = \text{NO}_2$  and  $\text{SO}_2$ .

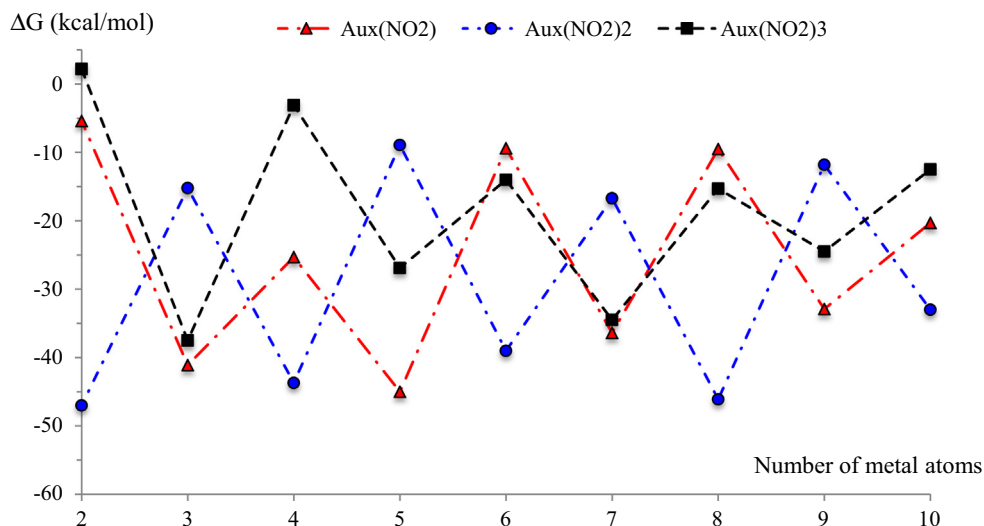


Fig. 7.  $\Delta G$  (kcal/mol) for the  $[\text{Au}_x-(\text{NO}_2)_{y-1}] + \text{NO}_2 \rightarrow [\text{Au}_x-(\text{NO}_2)_y]$  reaction;  $x = 2-10$  and  $y = 1-3$ .

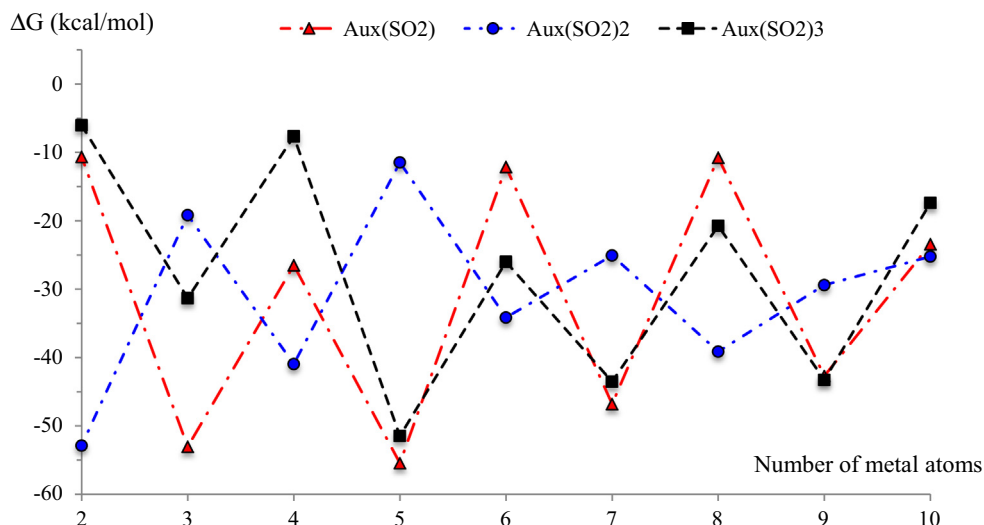


Fig. 8.  $\Delta G$  (kcal/mol) for the  $[\text{Au}_x-(\text{SO}_2)_{y-1}] + \text{SO}_2 \rightarrow [\text{Au}_x-(\text{SO}_2)_y]$  reaction;  $x = 2-10$  and  $y = 1-3$ .

this is not the case on the addition of the third molecule. Similar results were found for  $\text{Au}_4$ . For gold clusters with 6, 8 and 10 atoms, less exergonic reactions are evident on the third addition than the second one. In the case of gold clusters with 3, 5, 7 and 9 atoms, results are reversed (third addition is more exergonic than second addition, and first addition is the most exergonic). Regardless of which is more exergonic, the most important result is that in thermodynamic terms, all gold clusters are capable of trapping up to three molecules from these contaminants.

Fig. 9 reports the optimized structures of the most stable structures of  $\text{Au}_{20}$  with one, two and three molecules of  $\text{NO}_2$  and  $\text{SO}_2$ . Gibbs free energies are also presented in the Figure. For all geometries, gold cluster maintains a structure similar to that of the bare cluster, and molecules are molecularly bonded. All the reactions are exergonic, and are generally less exergonic than the corresponding reactions for smaller gold clusters. Apparently, as the size of the cluster increases, exergonicity decreases. In summary, successive additions of  $\text{NO}_2$  and  $\text{SO}_2$  in gold clusters are exergonic,

making these systems efficacious for trapping these atmospheric pollutants.

#### 4. Concluding remarks

This investigation is a theoretical study of the reactivity of small metal clusters (Cu, Ag and Au) with air pollutant molecules ( $\text{NO}_2$  and  $\text{SO}_2$ ). The formation energies indicate that these small metal clusters could act as air pollutant hunters, as reactions are exergonic and thus thermodynamically feasible. Cu clusters present the most exergonic reactions, followed by Ag and Au, respectively. Furthermore there is even-odd alternation in the Gibbs free energy of the addition reactions. Au clusters were used to study successive additions and results show that Au clusters are capable of trapping up to three air pollutant molecules ( $\text{NO}_2$  and  $\text{SO}_2$ ). These results may serve as an important guide for further experimental and theoretical studies.

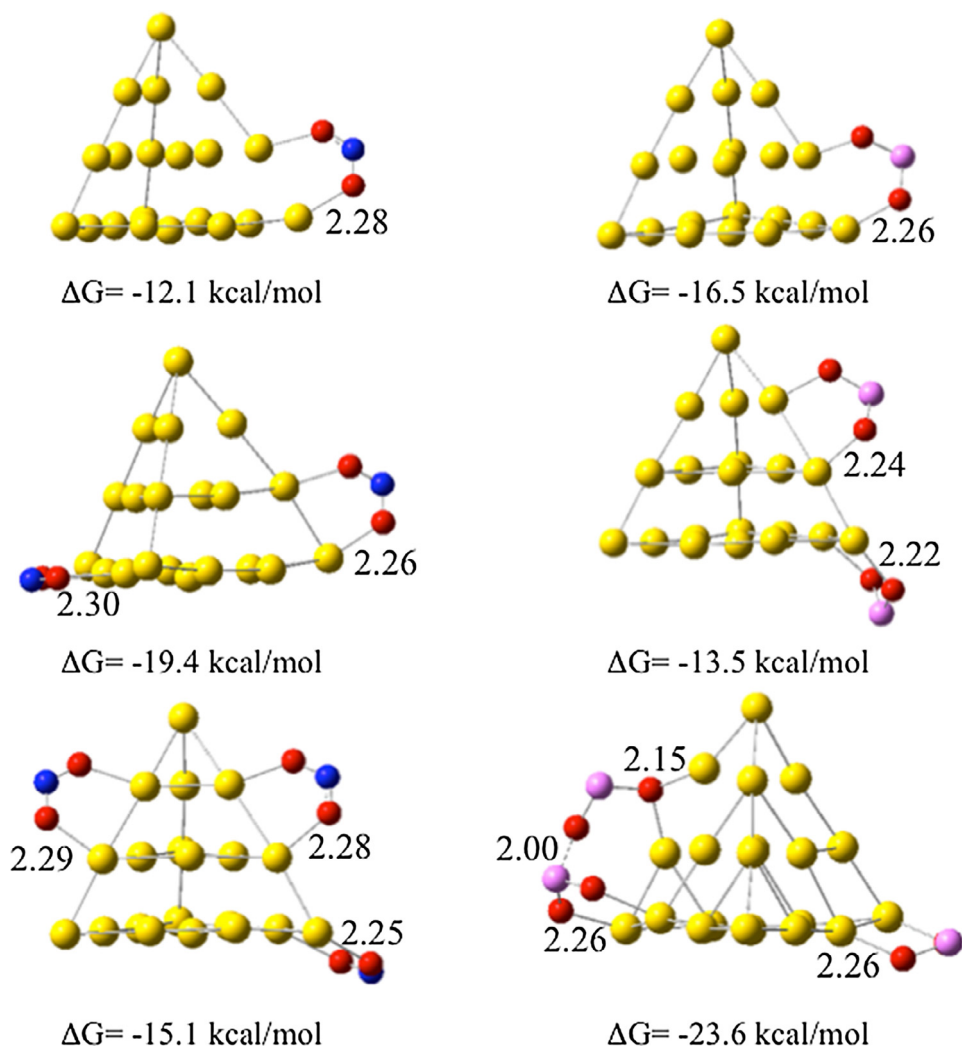


Fig. 9. Optimized structures for  $Au_{20}(R)_y$  systems,  $R = NO_2$  and  $SO_2$  and  $y = 1-3$ . We include the  $\Delta G$  (kcal/mol) of reaction.

## Acknowledgements

This study was funded by DGAPA-PAPIIT, Consejo Nacional de Ciencia y Tecnología (CONACyT), and resources provided by the Instituto de Investigaciones en Materiales (IIM). This work was carried out using a NES supercomputer, provided by Dirección General de Cómputo y Tecnologías de Información y Comunicación (DGTIC), Universidad Nacional Autónoma de México (UNAM). We would like to thank the DGTIC of UNAM for their excellent and free supercomputing services and Caroline Karlake (Masters, Social Anthropology, Cambridge University, England) for reviewing the grammar and style of the text in English. The authors would like to acknowledge Oralia L Jiménez A., María Teresa Vázquez, Alberto López Vivas and Caín González for their technical support. MR thanks CONACyT for the PhD scholarship (387687).

## References

- [1] Z. Luo, A.W. Castleman Jr., S.N. Khanna, Reactivity of metal clusters, *Chem. Rev.* 116 (2016) 14456–14492.
- [2] G. Dietrich, S. Kruckeberg, K. Lutzenkirchen, L. Schweikhard, C. Walther, The interaction of gold clusters with methanol molecules: infrared photodissociation of mass-selected  $Au_n^+(CH_3OH)_m$ , *J. Chem. Phys.* 112 (2000) 752–760.
- [3] V.A. Spasov, T.H. Lee, K.M. Ervin, Threshold collision induced dissociation of anionic copper clusters and copper cluster monocarbonyls, *J. Chem. Phys.* 112 (2000) 1713–1720.
- [4] K. Mondal, D. Manna, T.K. Ghanty, A. Banerjee, Significant modulation of CO adsorption on bimetallic  $Au_{19}Li$  cluster, *Chem. Phys. Phys. Chem.* 428 (2014) 75–81.
- [5] W.T. Wallace, A.J. Leavitt, R.L. Whetten, Comment on: the adsorption of molecular oxygen on neutral and negative  $Au_n$  clusters ( $N=2-5$ ), *Chem. Phys. Lett.* 368 (2002) 774–777.
- [6] M.L. Kimble, A.W. Castleman Jr., R. Mitrić, C. Bürgel, V. Bonačić-Koutecký, Reactivity of atomic gold anions toward oxygen and the oxidation of CO: experiment and theory, *J. Am. Chem. Soc.* 126 (2004) 2526–2535.
- [7] M.L. Kimble, A.W. Castleman Jr., C. Bürgel, V. Bonačić-Koutecký, Interactions of CO with  $Au_nO_m^-$  ( $n \geq 4$ ), *Int. J. of Mass Spectr.* 254 (2006) 163–167.
- [8] M.L. Kimble, N.A. Moore, A.W. Castleman Jr., C. Bürgel, R. Mitrić, V. Bonačić Koutecký, Reactivity of anionic gold oxide clusters towards CO: experiment and theory, *Eur. Phys. J. D* 43 (2007) 205–208.
- [9] W.T. Wallace, R.L. Whetten, Carbon monoxide adsorption on selected gold clusters: highly size-dependent activity and saturation compositions, *J. Phys. Chem. B* 104 (2000) 10964–10968.
- [10] S.A. Varganov, R.M. Olson, M.S. Gordon, H. Meitu, The interaction of oxygen with small gold cluster, *J. Chem. Phys.* 119 (2003) 2531–2537.
- [11] X. Ding, Z. Li, J. Yang, J.G. Hou, Q.J. Zhu, Adsorption energies on molecular oxygen on Au clusters, *J. Chem. Phys.* 120 (2004) 9594–9600.
- [12] E.S. Kryachko, F. Remacle, The gold-ammonia bonding patterns of neutral and charged complexes  $Au_m^{0\pm 1}-(NH_3)_n$ . Bonding and charge alternation, *J. Chem. Phys.* 127 (2007) 194305–1–11.
- [13] H.J. Zhai, B. Kiran, B. Dai, J. Li, L.S. Wang, Unique CO chemisorption properties of gold hexamer:  $Au_6(CO)_n^-$  ( $n = 0-3$ ), *J. Am. Chem. Soc.* 127 (2005) 12098–12106.



- [14] D.H. Wells Jr., W.N. Delgass, K.T. Thomson, Density functional theory investigation of gold cluster geometry and gas-phase reactivity with O<sub>2</sub>, *J. Chem. Phys.* 117 (2002) 10597.
- [15] G. Mazzzone, I. Rivalta, N. Russo, E. Sicilia, Interaction of CO with PdAu(111) and PdAu(100) bimetallic surfaces: a theoretical cluster model study, *J. Phys. Chem. C* 112 (2008) 6073–6081.
- [16] G.E. Johnson, N.M. Reilly, E.C. Tyo, A.W. Castleman Jr., Gas-phase reactivity of gold oxide cluster cations with CO, *J. Phys. Chem. C* 112 (2008) 9730–9736.
- [17] C. Bürgel, N.M. Reilly, G.E. Johnson, R. Mitrić, M.L. Kimble, A.W. Castleman Jr., V. Bonačić-Koutecký, Influence of charge state on the mechanism of CO oxidation on gold clusters, *J. Am. Chem. Soc.* 130 (2008) 1694–1698.
- [18] M.B. Knickelbein, Electronic shell structure in the ionization potentials of copper clusters, *Chem. Phys. Lett.* 192 (1992) 129–134.
- [19] P. Calaminici, A.M. Koster, N. Russo, D.R. Salahub, A density functional study of small copper clusters: Cu<sub>n</sub> (n < 5), *J. Chem. Phys.* 105 (1996) 9546–9556.
- [20] J. Ma, X. Cao, X. Xing, X. Wang, J.H. Parks, Adsorption of O<sub>2</sub> on anionic silver clusters: spins and electron binding energies dominate in the range up to nano sizes, *Phys. Chem. Chem. Phys.* 18 (2016) 743–748.
- [21] B. Yoon, H. Häkkinen, U. Landman, Interaction of O<sub>2</sub> with gold clusters: molecular and dissociative adsorption, *J. Phys. Chem. A* 107 (2003) 4066–4071.
- [22] B.E. Salisbury, W.T. Wallace, R.L. Whetten, Low-temperature activation of molecular oxygen by gold clusters: a stoichiometric process correlated to electron affinity, *Chem. Phys.* 262 (2000) 131–141.
- [23] M. Reina, A. Martínez, How the presence of metal atoms and clusters can modify the properties of Silybin? A computational prediction, *Comp. Theor. Chem.* 1099 (2017) 174–184.
- [24] M. Reina, A. Martínez, Silybin interacting with Cu<sub>4</sub>, Ag<sub>4</sub> and Au<sub>4</sub> clusters: do these constitute antioxidant materials?, *Comp. Theor. Chem.* 1112 (2017) 1–9.
- [25] H. Grönbeck, A. Rosén, Analysis of the odd-even alternation of simple metal clusters, *Z. Phys. D.* 36 (1996) 153–157.
- [26] Z. Luo, G.U. Gamboa, J.C. Smith, A.C. Reber, J.U. Reveles, S.N. Khanna, A.W. Castleman Jr., Spin accommodation and reactivity of silver clusters with oxygen: the enhanced stability of Ag<sub>13</sub>, *J. Am. Chem. Soc.* 134 (2012) 18973–18978.
- [27] T.H. Lee, K.M. Ervin, Reactions of copper group cluster anions with oxygen and carbon monoxide, *J. Phys. Chem.* 98 (1994) 10023–10031.
- [28] E. Florez, W. Tiznado, F. Mondragón, P. Fuentealba, Theoretical study of the interaction of molecular oxygen with copper clusters, *J. Phys. Chem. A* 109 (2005) 7815–7821.
- [29] A. Martínez, Size matters, but is being planar any relevance? Electron donor-acceptor properties of neutral gold clusters up to 20 atoms, *J. Phys. Chem. C* 114 (2010) 21240–21246.
- [30] M. Reina, A. Martínez, Free radicals interacting with Cu, Ag and Au clusters, *Comp. Theor. Chem.* 1120 (2017) 24–33.
- [31] E.-B. Andrade, A. Martínez, Free radical scavenger properties of metal-fullerenes: C<sub>60</sub> and C<sub>82</sub> with Cu, Ag and Au (atoms and tetramers), *Comp. Theor. Chem.* 1115 (2017) 127–135.
- [32] M.C. Daniel, D. Astruc, Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, *Chem. Rev.* 104 (2004) 293–346.
- [33] X. Huang, P.K. Jain, I.H. El-Sayed, M.A. El-Sayed, Gold nanoparticles: interesting optical properties and recent applications in cancer diagnostics and therapy, *Nanomedicine* 2 (2007) 681–693.
- [34] P. Schwerdtfeger, Gold goes nano—from small clusters to low-dimensional assemblies, *Angew. Chem.* 42 (2003) 1892–1895.
- [35] I. Katakuse, T. Ichihara, Y. Fujita, T. Matsuo, T. Sakurai, H. Matsuda, Mass distributions of copper, silver and gold clusters and electronic shell structure, *Int. J. Mass Spectrom. Ion Process.* 67 (1985) 229–236.
- [36] J. Hagen, L.D. Socaciu, M. Eljazyfer, U. Heiz, T.M. Bernhardt, L. Woste, Coadsorption of CO and O<sub>2</sub> on small free gold cluster anions at cryogenic temperatures: model complexes for catalytic CO oxidation, *Phys. Chem. Chem. Phys.* 4 (2002) 1707–1709.
- [37] J. Hagen, L.D. Socaciu, J. Le Roux, D. Popolan, T.M. Bernhardt, L. Woste, R. Mitrić, H. Noack, V. Bonačić-Koutecký, Cooperative effects in the activation of molecular oxygen by anionic silver clusters, *J. Am. Chem. Soc.* 126 (2004) 3442–3443.
- [38] S.M. Lang, T.M. Bernhardt, Cooperative and competitive coadsorption of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> on Au<sub>x</sub><sup>-</sup> (x = 3,5), *J. Chem. Phys.* 131 (2009) 024310.
- [39] M. Goldberg, R. Langer, J. Xinqiao, Nanostructured materials for applications in drug delivery and tissue engineering, *J. of Biomater. Sci., Polymer Ed.* 18(3) (2007) 241–268.
- [40] O. Kayser, A. Lemke, N. Hernandez-Trejo, The impact of nanobiotechnology on the development of new drug delivery systems, *Curr. Pharm. Biotechnol* 6 (2005) 3–5.
- [41] R. Madhanraj, M. Eyini, P. Balaji, Antioxidant assay of gold and silver nanoparticles from edible basidiomycetes mushroom fungi, *Free Rad. and Antioxid.* 7(2) (2017) 137–145.
- [42] L.M. Gaetke, C.K. Chow, Copper toxicity, oxidative stress, and antioxidant nutrients, *Toxicology* 189 (2003) 147–163.
- [43] D. Guo, L. Zhu, Z. Huang, H. Zhou, Y. Ge, W. Ma, J. Wu, X. Zhang, X. Zhou, Y. Zhang, Y. Zhao, N. Gu, Anti-leukemia activity of PVP-coated silver nanoparticles via generation of reactive oxygen species and release of silver ions, *Biomaterials* 34 (2013) 7884–7894.
- [44] Y.S. Chen, Y.C. Hung, I. Liao, G.S. Huang, Assessment of the in vivo toxicity of gold nanoparticles, *Nanoscale Res. Lett.* 4 (2009) 858–864.
- [45] C.M. Goodman, C.D. McCusker, T. Yilmaz, V.M. Rotello, Toxicity of gold nanoparticles functionalized with cationic and anionic side chains, *Bioconjug. Chem.* 15 (4) (2004) 897–900.
- [46] P. Ghosh, G. Han, M. De, C.K. Kim, V.M. Rotello, Gold particles in delivery applications, *Adv. Drug Deliv. Rev.* 60 (2008) 1307–1315.
- [47] J. Chen, D. Wang, J. Xi, L. Au, A. Siekkinen, A. Warsen, Z.Y. Li, H. Zhang, Y. Xia, X. Li, Immuno gold nanocages with tailored optical properties for targeted photothermal destruction of cancer cells, *Nano Lett.* 7 (5) (2007) 1318–1322.
- [48] N. Greenberg, R.S. Carel, E. Derazne, H. Bibi, M. Shpriz, D. Tzur, B.A. Portnov, Different effects of long-term exposures to SO<sub>2</sub> and NO<sub>2</sub> air pollutants on asthma severity in young adults, *J. Toxicol. Environ. Health A* 79 (8) (2016) 342–345.
- [49] N.A.B. Mabahwi, O.L.H. Leh, D. Omar, Human health and wellbeing: Human health effect of air pollution, *Procedia - Social and Behavior. Sci.* 153 (2014) 221–229.
- [50] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, 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, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 09, Revision A.08 Inc. Wallingford, CT, 2009.
- [51] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* 120 (2008) 215.
- [52] G.A. Petersson, A. Bennett, T.G. Tensfeldt, M.A. Al-Laham, W.A. Shirley, J.A. Mantzaris, A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row atoms, *J. Chem. Phys.* 89 (1988) 2193–2198.
- [53] G.A. Petersson, M.A. Al-Laham, A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms, *J. Chem. Phys.* 94 (1991) 6081–6090.
- [54] A.D. McLean, G.S. Chandler, Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11–18, *J. Chem. Phys.* 72 (1980) 5639–5648.
- [55] K. Raghavachari, J.S. Binkley, R. Seeger, J.A. Pople, Self-consistent molecular orbital methods. 20. Basis set for correlated wave-functions, *J. Chem. Phys.* 72 (1980) 650–654.
- [56] 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.
- [57] 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.
- [58] 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.
- [59] K. Jug, B. Zimmermann, P. Calaminici, A. Köster, Structure and stability of small copper clusters, *J. Chem. Phys.* 116 (2002) 4497–4507.
- [60] R. Fournier, Theoretical study of the structure of silver clusters, *J. Chem. Phys.* 115 (2001) 2165–2169.