# Free radicals interacting with Cu, Ag and Au clusters

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## ARTICLE INFO

## ABSTRACT

We investigated free radical scavenger capacity of small neutral Cu, Ag and Au clusters (Cu, Ag and Au up to ten atoms, and $Au_{20}$), using three molecules ($\cdot$OH, $\cdot$OOH, $\cdot$OCH$_3$) and two reaction mechanisms (Electron Transfer and Radical Adduct Formation). Principally this indicates that metal clusters are good free radical scavengers. They are good electron donors and the radical adduct formation reaction is thermodynamically feasible. Here, we show how Molecular Electrostatic Potential is very useful for determining the active site of the cluster in terms of interaction with the free radical. This investigation affirms that free radicals interact with the balanced electron density zone of the cluster. This may be very important for further studies that contemplate more than one free radical bonded to the metal clusters. These findings should serve as a significant guide for experimentalists when attempting to analyze the effectiveness of small Cu, Ag and Au clusters, as antioxidant materials.

## 1. Introduction

The chemical reactivity of metal clusters has been extensively studied providing useful information and interesting results [1–65]. It is widely recognized that the properties of clusters cannot be deduced by linear extension from atoms to bulk, as clusters present a very high surface-to-volume ratio and unique geometric shapes that critically influence their electronic properties.

Reactivity of metal clusters has been studied extensively for several reactions involving the adsorption of small molecules ($N_2$, CO, $H_2$, NO, $O_2$, $H_2O$, $NH_3$); the interaction with DNA and RNA bases; the formation of gold-ammonia complexes for medical and catalysis purposes; and research concerning the potential of these materials as optoelectronic devices [6–52]. Coinage metals (Cu, Ag and Au) in particular, present an electronic configuration with a closed *d* shell and a single *s* valence electron. With reference to this, it was reported that they react with halogens following the same mechanism as alkali metals [33–35]. The reactions of anionic $Cu_x$, $Ag_x$ and $Au_x$ with CO and $O_2$ indicate that gold clusters are more reactive than the others [10,36–41]. Among molecules used to analyze the reactivity of metal clusters, specific information can be derived from those molecules that are almost non-reactive, such as $N_2$ [42–47]. Likewise, using highly reactive molecules may offer interesting results that elucidate the chemical reactivity of these systems. The study of free radicals as molecules

that react with metal clusters may provide important information, as these represent very reactive species with one unpaired electron.

Some reactivity models reported in the literature help explain the reaction mechanisms of metal clusters. *Harpoon* mechanism has been successfully used to explain reactions between coinage metals and halogens [59]. Spin excitation studies are important for determining the cluster reactivity of metals clusters with oxygen, especially for Cu cluster anions [60]. The Complementary Active Sites (CAS) mechanism takes into account Lewis acidity and contributes to rationalizing the interaction between polar molecules and metal clusters [61,62]. Finally, there are reports, which consider the reactivity of free radicals with systems formed by Cu, Ag and Au clusters interacting with organic molecules and $C_{60}$ [63–65]. In spite of all these investigations, there are no reports describing bare coinage metal clusters reacting with centered oxygen free radicals. The information gathered so far does not fully investigate the reactivity of coinage metal clusters towards free radicals and nor has any mechanism been proposed that attempts to explain the reactivity between metal clusters and free radicals. For this reason, in this theoretical investigation, we aim to analyze the reactivity of Cu, Ag and Au clusters (up to ten atoms) towards oxygen centered free radicals ($\cdot$OH, $\cdot$OOH and $\cdot$OCH$_3$) in order to model the reaction mechanism. $Au_{20}$ is also investigated, as it is interesting to analyze how reactivity and electronic properties change due to cluster size and shape. Free radical scavenging reactivity is studied with reference to Electron Transfer (ET) and Radical Adduct Formation (RAF) mechanisms. Full Electron

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Donor-Acceptor Map (FEDAM) [66,67] and Molecular Electrostatic Potential (MEP) are employed to assess the reactivity of these metal clusters and to model a possible reaction mechanism.

## 2. Computational details

Geometry optimization and electronic calculations were performed with Gaussian 09 implementation [68]. Initial geometries were fully optimized at M06/LanL2DZ level of theory in gas phase [69–76]. In order to verify local minima, harmonic analyses were calculated (zero imaginary frequencies). Initial geometries for $Cu_x$, $Ag_x$ and $Au_x$ clusters (x = 2–10 and $Au_{20}$) were described in previous reports [12,77,78].

Vertical ionization energy (*I*) and vertical electron affinity (*A*) for analysis of the ET mechanism were calculated from the single point energy of the corresponding cationic and anionic systems, using the optimized structure of the neutrals at the same level of theory, in conjunction with the SMD continuum model and using water to mimic a polar environment [79].

FEDAM (Fig. 1) is a useful tool that has been described previously [66,67]. *I* and *A* of each system are plotted in this map, enabling us to classify systems as either electron donors or acceptors. Electrons will be transferred from molecules located down to the left of the map (good electrons donors) to those molecules that are up to the right (good electron acceptors).

To investigate the RAF mechanism, Gibbs free energy values were calculated applying the following reaction scheme:

$$M_x + R^{\cdot} \rightarrow [M_x - R]^{\cdot}$$
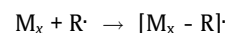
$$\Delta G = G([M_x - R^{\cdot}]) - G(M_x) - G(R^{\cdot})$$

M is Cu, Ag or Au, *x* corresponds to the number of metal atoms (2–10); $R^{\cdot}$ is the free radical ($^{\cdot}OH$, $^{\cdot}OOH$ and $^{\cdot}OCH_3$); $[M_x\text{-}R]$ is the free radical adduct. The lowest spin multiplicity (singlet or doublet) is the most stable for all the systems being studied. $Au_{20}$ is also investigated to analyze how the reactivity properties change as the number of atoms in the cluster increases.

To analyze the RAF mechanism, it is important to predict the most reactive sites for the interaction between metal clusters and free radicals. Molecular Electrostatic Potential (MEP) was analyzed for this purpose. MEP is obtained for $M_x$ (M = Cu, Ag and Au, x = 2–10 and $Au_{20}$) using total electron density. The red color of

MEP corresponds to high electron density regions, blue color to low electron density and green color to balanced electron density.

## 3. Results and discussion

Fig. 2 presents the optimized $M_x$ clusters (M = Cu, Ag, Au; x = 2–10) and some bond distances are also included. Most stable geometries were previously reported [12,77,78]. In this study, we re-optimized these structures in order to be able to analyze reactivity. As reported previously, the most stable structures of Cu and Ag clusters up to six atoms, and Au clusters up to ten atoms, present planar structures. As predicted, Cu clusters present shorter bond distances than Ag and Au systems.

In order to analyze the ET mechanism, it is important to define the direction of the electron transfer. To this end, the FEDAM is a very useful tool. The FEDAM of these molecules is reported in Fig. 3. As already explained, electrons must be transferred from the systems located down to the left (good electron donors) to those that are located up to the right (good electron acceptors). According to the results reported in Fig. 3, electron transfer is from metal clusters to free radicals, *i.e.* in the case of free radicals, metal clusters are electron donors and may scavenge free radicals by donating an electron. The best electron donors are copper clusters and the best electron acceptors are gold clusters.

For the RAF mechanism, it is important to determine the reactive site for the interaction between the metal cluster and the free radical. It is possible to use the MEP for this purpose. MEP is a graphic tool that made it possible for us to characterize the atoms according to their electron density. Fig. 4 reports the MEP for the most stable optimized Cu, Ag and Au clusters. Fig. 5 presents the optimized geometry and MEP of $Au_{20}$. This structure has been previously reported as the most stable [12]. Most of the blue areas, which are electron deficient zones, are located at the vertexes of the structures. Red areas correspond to electron rich zones at the middle of the clusters, especially for Au systems. Finally, green areas that represent balanced electron density zones are mainly located in metal atoms that are found at the periphery of the clusters.

As metal clusters act as electron donors, it is reasonable to consider that the electron rich zones of the clusters are the most suitable for forming a bond with free radicals. Adhering to this idea, we decided to use initial geometries for the radical adducts with one free radical bonded to one metal atom of the cluster that corresponds to the MEP red zones. Surprisingly, initiating with these geometries, the optimized structures lead to dissociated products (the free radical molecule does not bond to the metal cluster) or to systems with negative frequencies (structures that are not minimum in the potential energy surface). In the light of these results, we decided to modify initial geometries and use structures where the free radical is bonded to a neutral zone of the cluster's MEP (green areas). With these initial geometries, the optimized structures that we obtained are those in Figs. 6–8 (for $[M_x\text{-}(OH)^{\cdot}]$, $[M_x\text{-}(OOH)^{\cdot}]$ and $[M_x\text{-}(OCH_3)^{\cdot}]$, respectively). The presence of the free radicals does not modify the planar or three-dimensional structure of the clusters. This is important as reactivity correlates with the shape of clusters [12,80–82]. For $[Au_N\text{-}R^{\cdot}]$, planar structures are the most stable except for $[Au_9\text{-}R^{\cdot}]$ systems, in which a slight distortion from the plane is observed. As expected, distances $M_x$-R are shorter for Cu systems compared to Ag and Au. Fig. 9 reports the interaction between $Au_{20}$ and free radicals. We include the most stable structure and also the second stable structure in this Figure. As can be seen, the energy difference is small for $[Au_{20}\text{-}OOH^{\cdot}]$ and $[Au_{20}\text{-}OCH_3]$ and both structures could be present in an experiment. For $[Au_{20}\text{-}OH^{\cdot}]$, $[Au_{20}\text{-}OOH^{\cdot}]$ and $[Au_{20}\text{-}OCH_3]$ systems, free radical molecules are bonded to atoms that
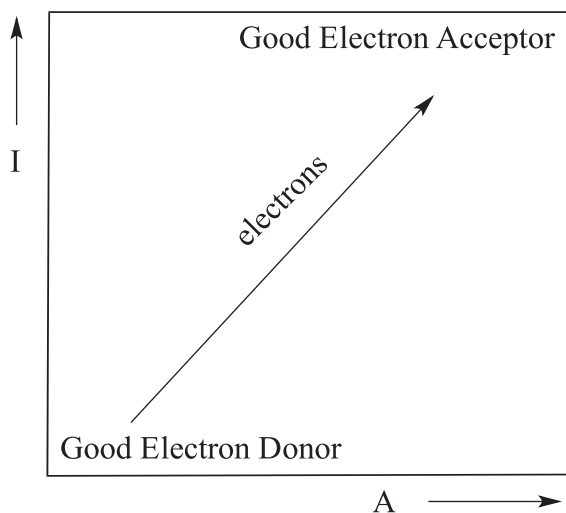


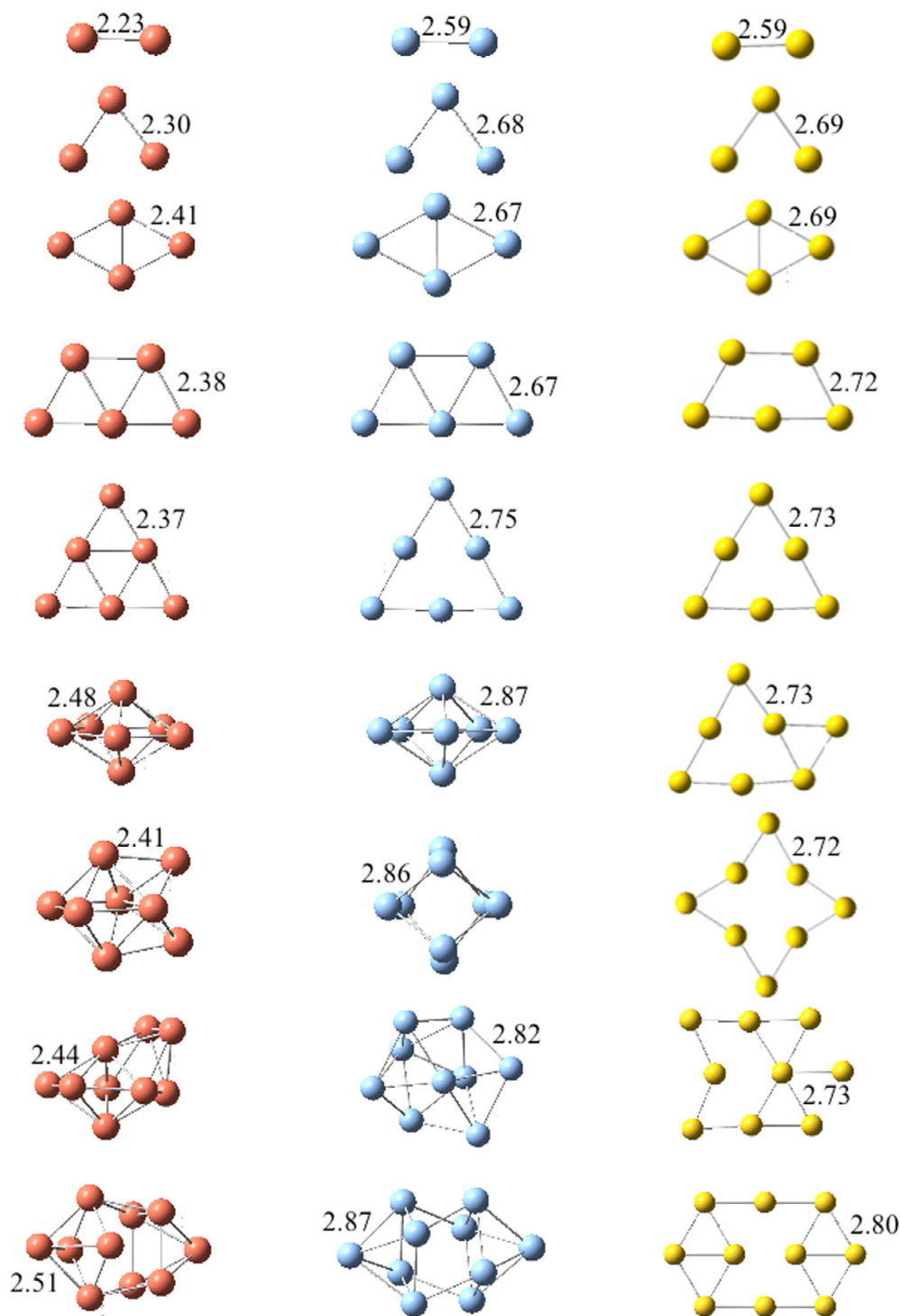**Fig. 1.** Full Electron Donor-Acceptor Map (FEDAM).

**Fig. 2.** Optimized structures of Cu (red), Ag (blue) and Au (yellow) clusters up to ten atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

correspond to green regions of the MEP. In all the most stable compounds of Au$_{20}$, the oxygen atom is bonded to two Au atoms.

In summary, the most stable compounds are those where the free radical is bonded to the atoms corresponding to the green areas of the MEP. This concurs with the idea that free radicals are neither nucleophiles nor electrophiles and would thus react with balanced electron density atoms. Metal clusters are electron donors but this characteristic does not in any way influence radical adduct formation.

To analyze the thermodynamics of the reaction, $\Delta G$ values were obtained for the most stable structures reported in Figs. 6–9. These results are reported in Table 1. Negative values indicate that the reactions are exergonic, and therefore, thermodynamically feasible. Values of Table 1 are all negative, indicating that all reactions are exergonic. Free radicals are spontaneously bonded to metal clusters. The most negative values are for Cu clusters interacting with ·OH. The interaction of metal clusters with ·OCH$_3$ and ·OOH is in all cases less exergonic. For ·OH, the most favored reactions
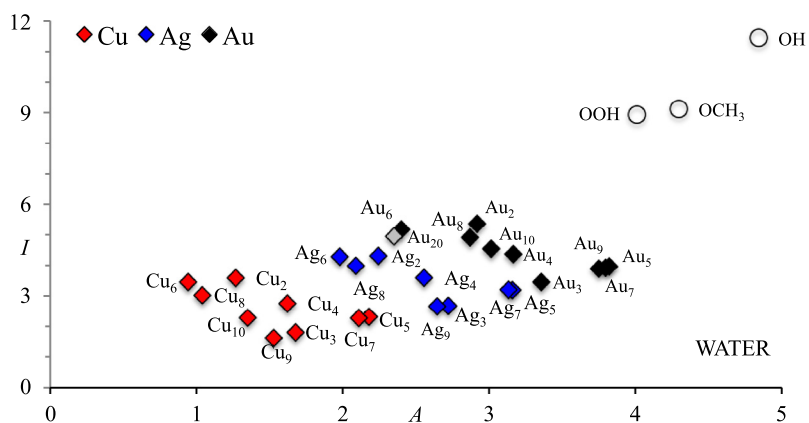
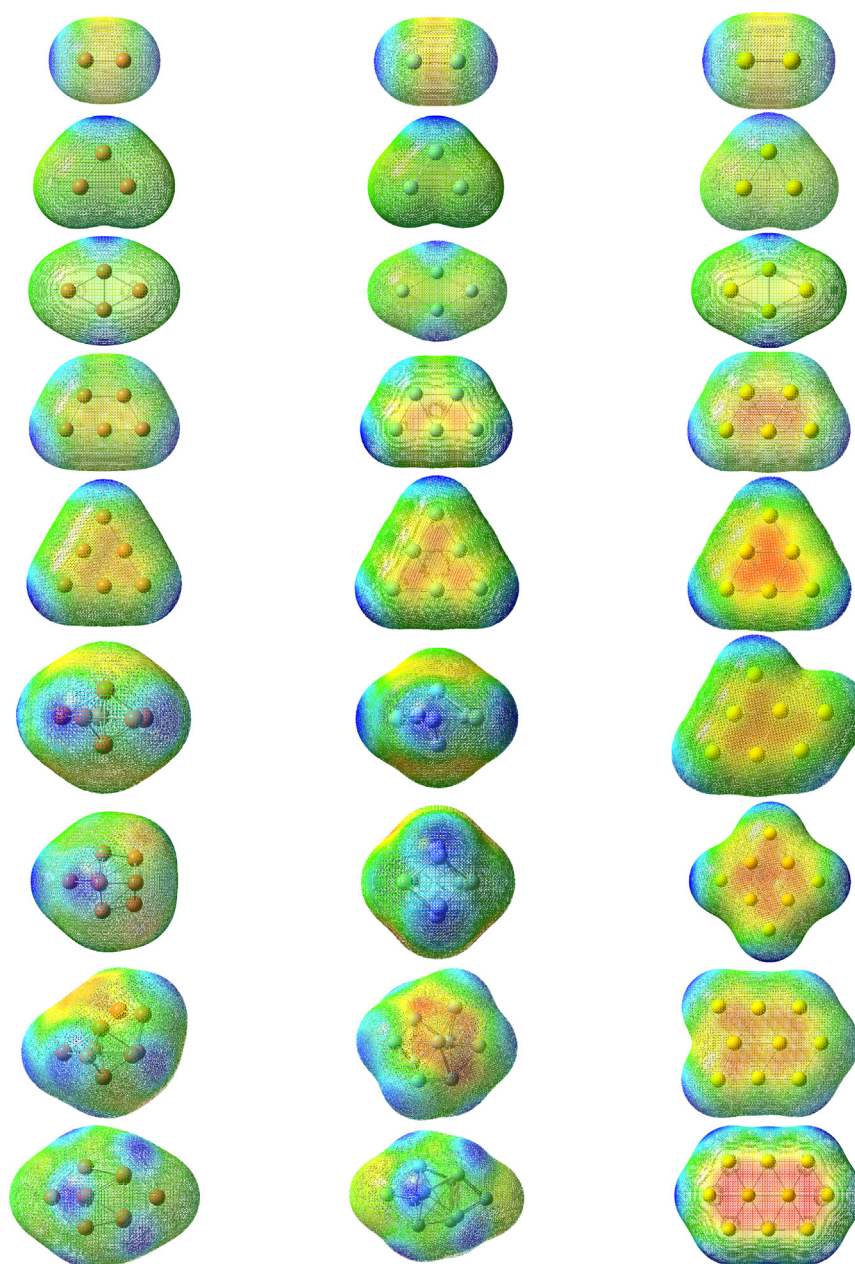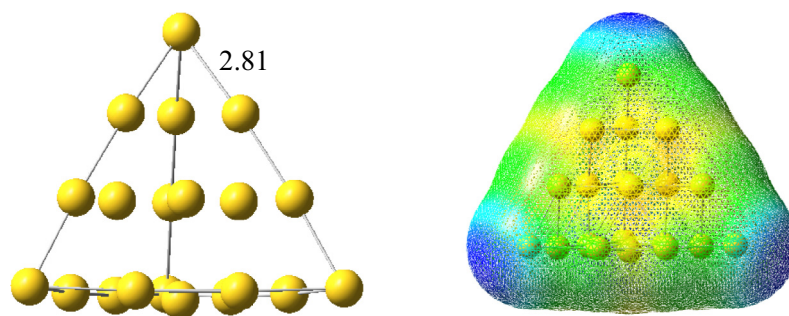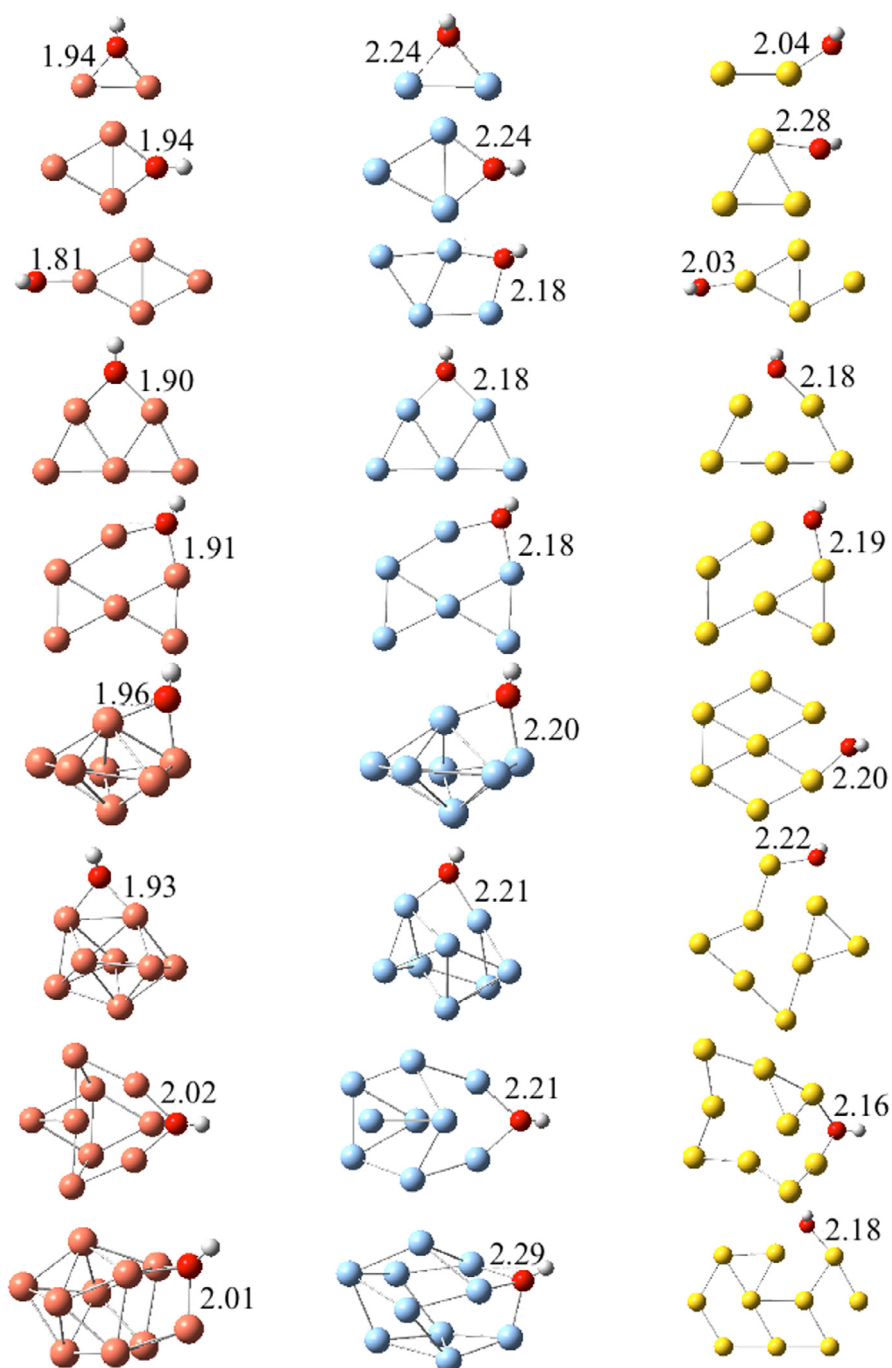**Fig. 3.** FEDAM with $M_x$ (M = Cu, Ag, Au; $x$ = 2–10) and $Au_{20}$. Free radicals are also included.



**Fig. 4.** Molecular Electrostatic Potential for optimized $M_x$ clusters (M = Cu, Ag, Au; $x$ = 2–10).

**Fig. 5.** Optimized structure and MEP of Au$_{20}$.



**Fig. 6.** Optimized structures for [M$_x$-OH$^-$] systems (M = Cu (red), Ag (blue), Au (yellow); $x$ = 2–10). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 7.** Optimized structures for [$M_x$-OOH$\cdot$] systems (M = Cu (red), Ag (blue), Au (yellow); $x = 2$–10). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
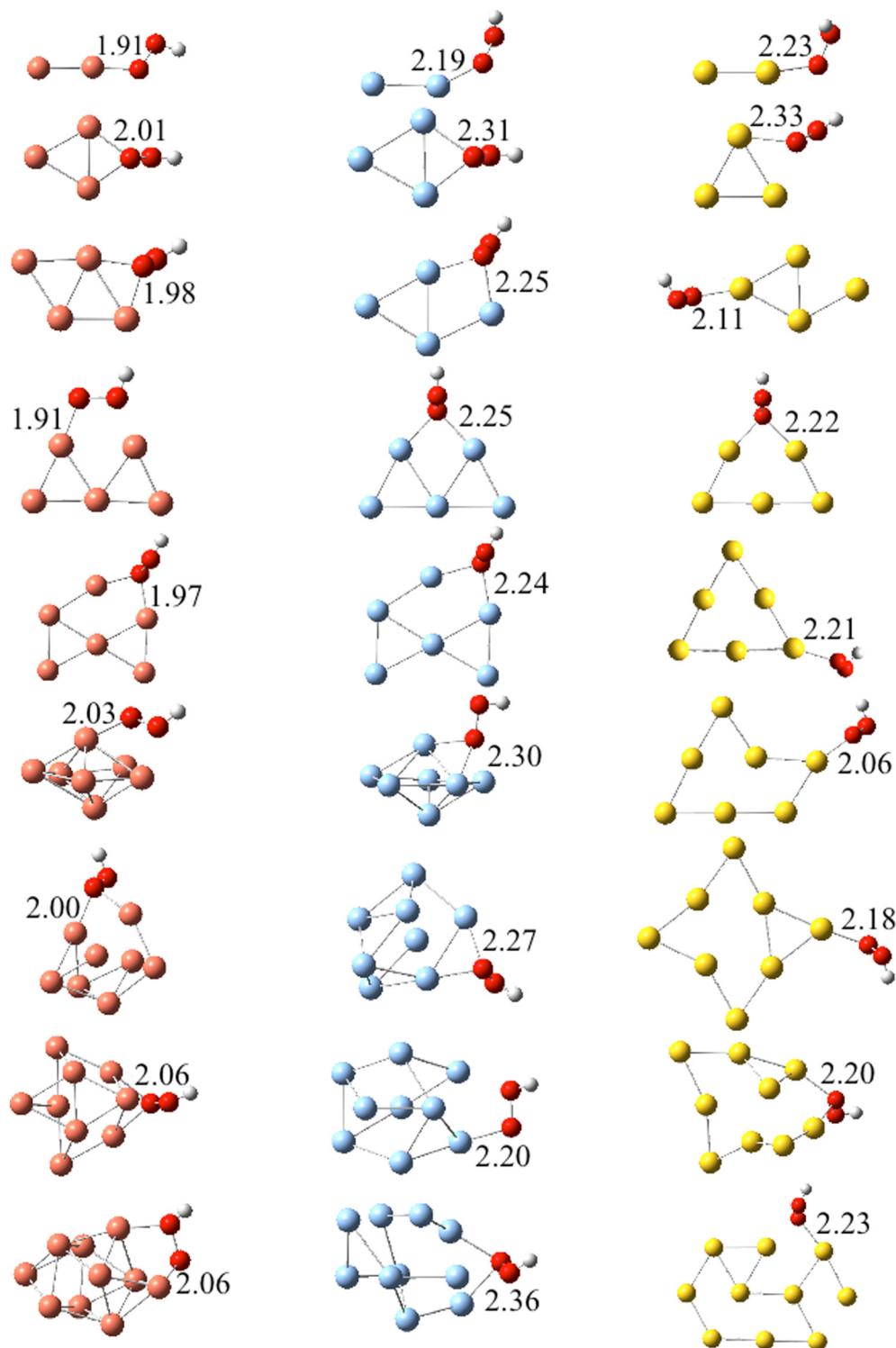
are [Cu$_5$-OH] and [Cu$_9$-OH] ($\Delta$G equal to $-86.1$ and $-82.4$ kcal/mol, respectively). [Cu$_9$-OOH] and [Cu$_5$-OOH] are the most stable compounds for $\cdot$OOH free radical ($\Delta$G equal to $-58.6$ and $-57.5$ kcal/mol, respectively). For $\cdot$OCH$_3$, [Cu$_5$-OCH$_3$] and [Cu$_3$-OCH$_3$] are the most favored systems ($\Delta$G equal to $-74.3$ and $-68.7$ kcal/mol, respectively). Generally, Cu clusters form the most stable complexes as they present the most negative $\Delta$G values and Au clusters form the least stable compounds. Table 1 reports also the results

for Au$_{20}$ that are similar to the other gold clusters. Au$_{20}$ was included since it is a well-known stable structure [12]. Comparing the results of Table 1 for clusters formed with 2–10 metal atoms (and Au$_{20}$), it is possible to say that, apparently, there is no correlation between reactivity and cluster size. Analyzing the results of Table 1, an odd-even alternation is found. Depending on the number of metal atoms, radical adducts are either closed-shell or open-shell systems. Clusters formed from an odd number of metal
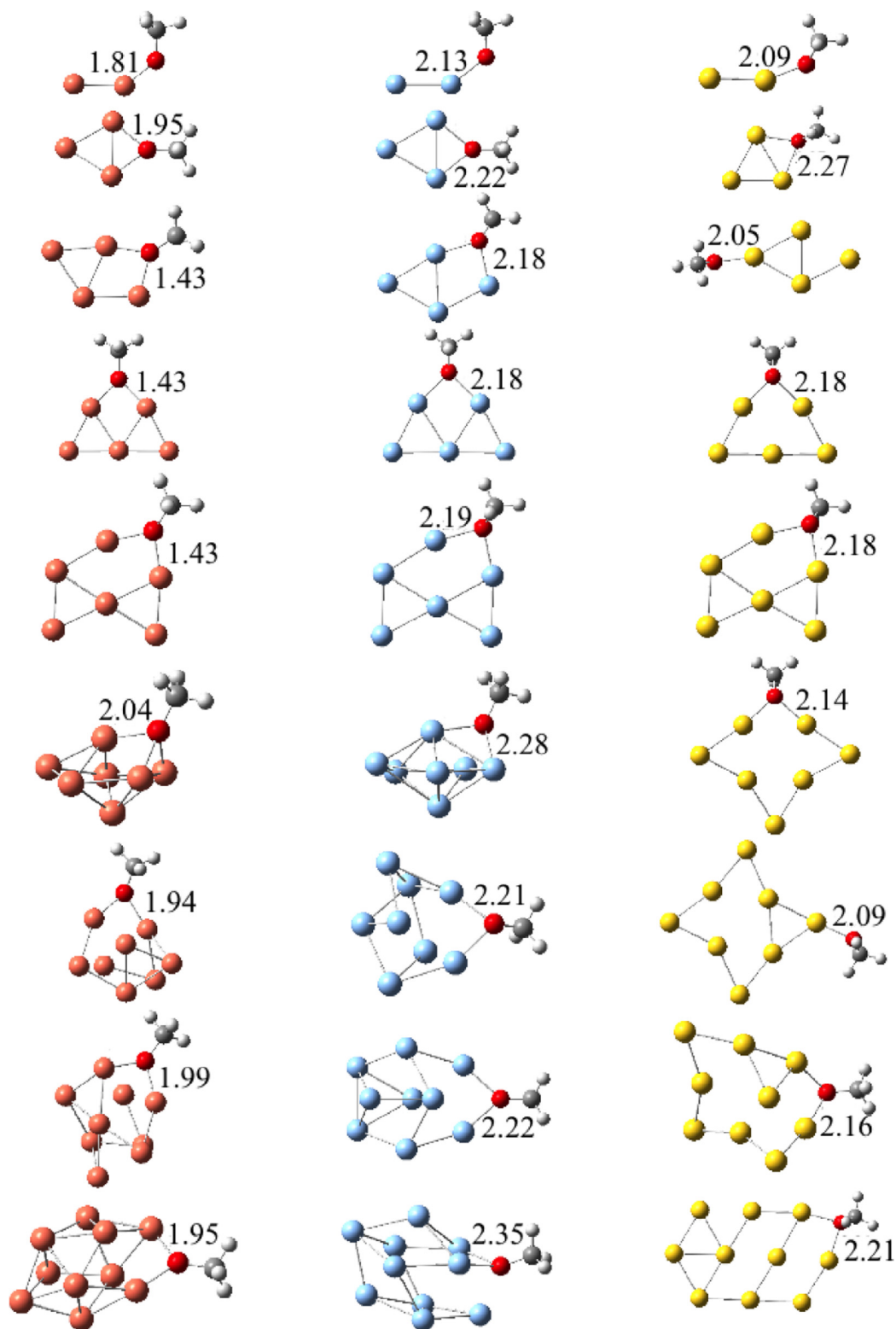
**Fig. 8.** Optimized structures for $[M_x\text{-}OCH_3]$ systems (M = Cu (red), Ag (blue), Au (yellow); $x$ = 2–10). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

atoms interacting with free radicals are closed-shell systems. These are more stable than open shell systems. Consequently, they have more negative ΔG values. Compounds with an even number of metal atoms interacting with free radicals are open-shell systems and have less negative Gibbs free energy values.

## 4. Concluding remarks

In this report, we present a theoretical study that assesses the reactivity of small clusters towards free radicals. The results of $Au_{20}$ indicate that there is no correlation between reactivity and
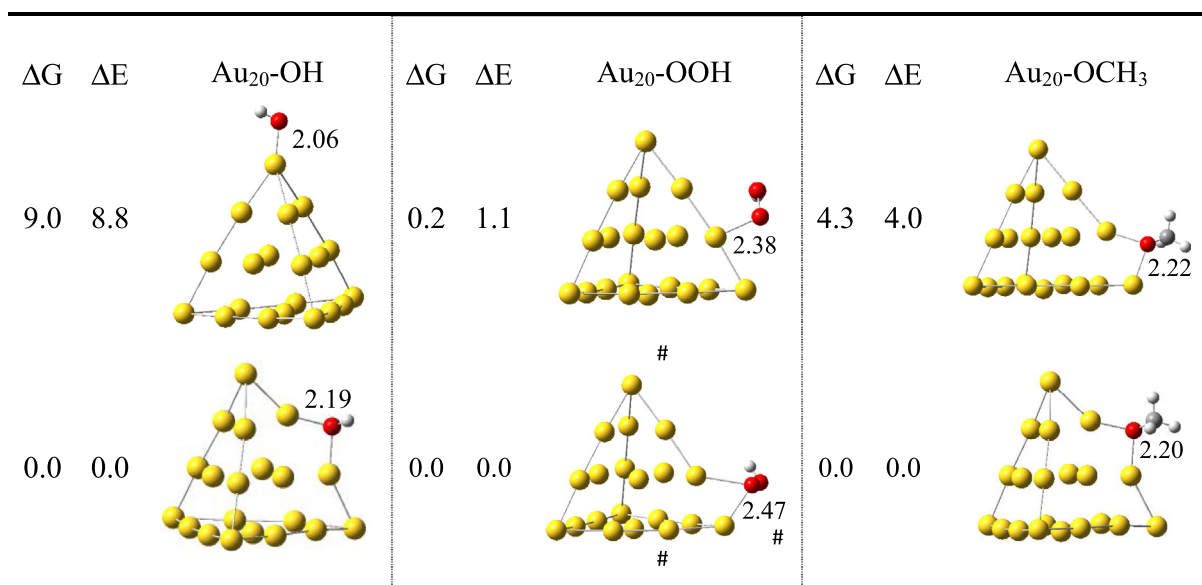
**Fig. 9.** Optimized structures for [Au$_{20}$-R$\cdot$] systems (R = $\cdot$OH, $\cdot$OOH and $\cdot$OCH$_3$).

**Table 1**

$\Delta G$ for the most stable structures according to the free radical adduct formation reaction. The equation used is the following [$\Delta G = G([Mx\text{-}R\cdot]) - G(Mx) - G(R\cdot)$]. Values are in kcal/mol.

| Size of the cluster | Copper clusters | | | Silver clusters | | | Gold clusters | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\cdot$OH | $\cdot$OOH | $\cdot$OCH$_3$ | $\cdot$OH | $\cdot$OOH | $\cdot$OCH$_3$ | $\cdot$OH | $\cdot$OOH | $\cdot$OCH$_3$ |
| M$_2$ | −45.0 | −8.9 | −28.8 | −28.8 | −5.9 | −13.9 | −18.4 | −3.2 | −13.6 |
| M$_3$ | −81.4 | −54.6 | −68.7 | −60.9 | −37.8 | −49.1 | −42.8 | −20.1 | −31.3 |
| M$_4$ | −66.1 | −39.0 | −52.9 | −47.3 | −24.9 | −34.5 | −24.4 | −4.0 | −−14.4 |
| M$_5$ | −86.1 | −57.5 | −74.3 | −65.3 | −41.2 | −51.8 | −57.1 | −31.0 | −44.9 |
| M$_6$ | −57.2 | −29.8 | −43.7 | −38.2 | −14.7 | −25.1 | −25.2 | −0.9 | −12.7 |
| M$_7$ | −63.3 | −43.6 | −52.6 | −48.7 | −25.5 | −37.5 | −50.4 | −15.8 | −45.4 |
| M$_8$ | −53.6 | −28.2 | −40.7 | −38.5 | −15.7 | −25.6 | −18.7 | −1.2 | −9.8 |
| M$_9$ | −82.4 | −58.6 | −66.6 | −59.9 | −34.7 | −47.5 | −46.5 | −21.1 | −34.3 |
| M$_{10}$ | −69.7 | −45.8 | −55.3 | −55.4 | −31.5 | −42.5 | −32.6 | −7.1 | −18.8 |
| M$_{20}$ | – | – | – | – | – | – | −27.6 | −1.7 | −16.0 |

gold cluster size. According to the FEDAM, metal clusters are electron donors and may scavenge free radicals by donating an electron. As expected, the best electron donors are copper clusters and the best electron acceptors are gold clusters. The formation energies of the systems under study indicates that the radical adduct formation reactions are exergonic and thermodynamically feasible. Cu clusters are the most reactive systems followed by Ag and Au clusters, respectively. Moreover, there is an even-odd alternation in the $\Delta G$ of formation. Closed shell systems are more stable than open shell systems, a factor that influences $\Delta G$ values.

Metal clusters are good free radical scavengers, as they are good electron donors and may form a free radical adduct. Molecular Electrostatic Potential is proposed to determine the active site of the cluster for these reactions with free radicals. This may be very important for further studies that consider more than one free radical bonded to the metal clusters. These findings should serve as a significant guide for experimentalists to test the potential of small Cu, Ag and Au metal clusters as antioxidants.

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