

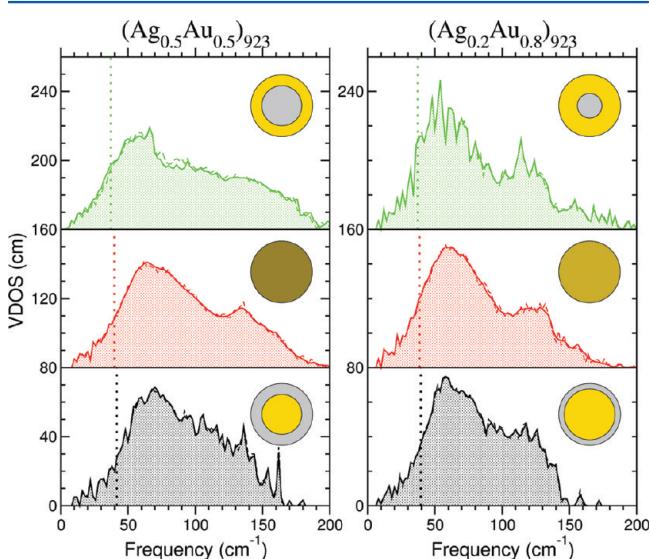
## Correction to “Influence of Size, Composition, and Chemical Order on the Vibrational Properties of Gold–Silver Nanoalloys”

F. Calvo\*

*J. Phys. Chem. C* 2011, 115 (36), 17730–17735; DOI: 10.1021/jp205656m

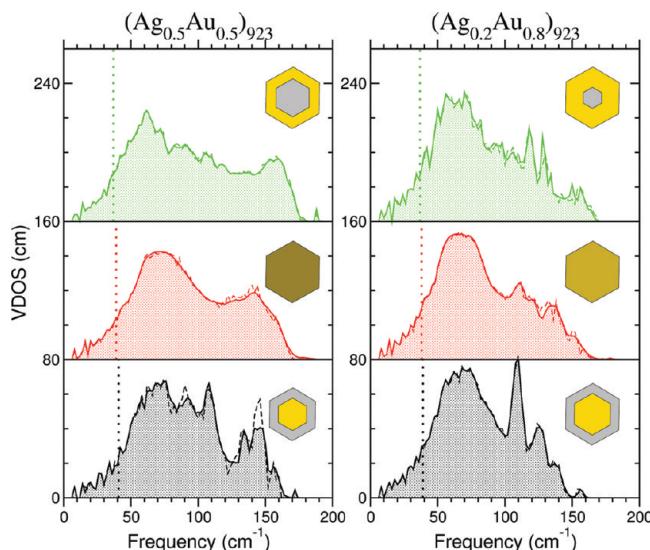
The calculations reported in the original paper<sup>1</sup> were erroneously performed after swapping the identities of the gold and silver atoms in the many-body potential and without swapping the atomic masses. All calculations have been repeated with the correct potential and masses, and the corrected figures are given below. The qualitative conclusions of the paper are not affected, although the quantitative details are, and we also provide the values of all fitting parameters for the new scaling laws.

The vibrational densities of states obtained for 923-atom icosahedral and cuboctahedral clusters still show very different shapes depending on chemical order, as seen in Figure 1 and Figure 2.



**Figure 1.** (Corrected) Densities of vibrational states of icosahedral, 923-atom Ag–Au nanoalloys, discretized into  $20\text{ cm}^{-1}$  bins, for 50% (left panel) and 20% (right) silver compositions and averaged over chemical disorder. The lowermost, central, and uppermost curves correspond to  $\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$ , alloy, and  $\text{Au}_{\text{shell}}\text{Ag}_{\text{core}}$  particles, respectively, with typical results from an individual homotop represented with dashed lines. Vertical dotted lines locate the breathing frequencies.

The revised calculations indicate a narrower range of variation for the breathing frequency as a function of silver concentration but a much stronger effect of chemical order, as depicted in Figure 3 in the case of the 5- and 6-shell icosahedral clusters and in Figure 4 for 6-shell cuboctahedral clusters. While the breathing frequency for the  $\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$  (respectively  $\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$ ) system still shows concave (respectively convex)



**Figure 2.** (Corrected) Densities of vibrational states of cuboctahedral, 923-atom Ag–Au nanoalloys, discretized into  $20\text{ cm}^{-1}$  bins, for 50% (left panel) and 20% (right) silver compositions and averaged over chemical disorder. The lowermost, central, and uppermost curves correspond to  $\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$ , alloy, and  $\text{Au}_{\text{shell}}\text{Ag}_{\text{core}}$  particles, respectively, with typical results from an individual homotop represented with dashed lines. Vertical dotted lines locate the breathing frequencies.

variations with increasing silver concentration, notice that the deviations relative to the alloyed case are larger than previously reported.<sup>1</sup>

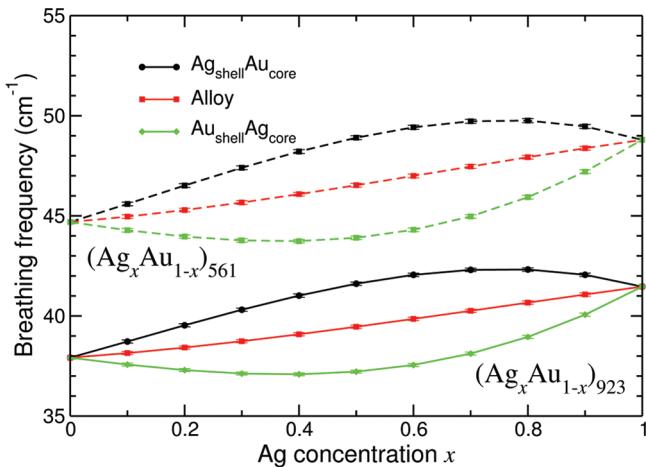
The size variations of the breathing frequency are still dominated by the inverse radius scaling, as illustrated in Figure 5 in the case of icosahedral clusters at equiconcentration.

It is still possible to express the general variations of the breathing frequency  $\omega_{\text{breathing}}$  as a function of size  $n$  and silver concentration  $x$  according to eq 5 of ref 1, which we repeat here for the sake of completion

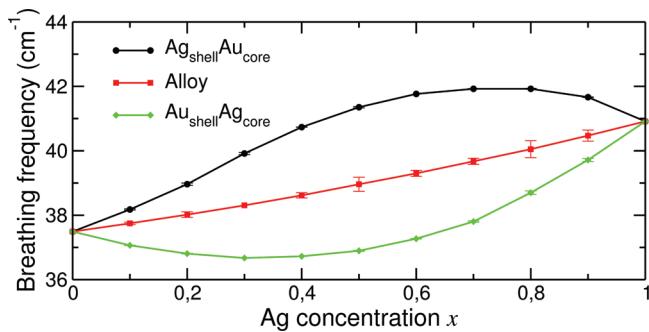
$$\begin{aligned}\omega_{\text{breathing}}(n, x) = & \omega(x)n^{-1/3} \times [1 + \alpha(x)n^{-1/3} \\ & + \gamma(x)n^{-2/3}]\end{aligned}\quad (1)$$

and the variations of the expansion parameters,  $\omega$ ,  $\alpha$ , and  $\gamma$ , for increasing concentration  $x$  are represented in Figure 6. Contrary to the original results, these variations are no longer so well described by a quadratic form in  $x$ , as stronger nonlinearities are

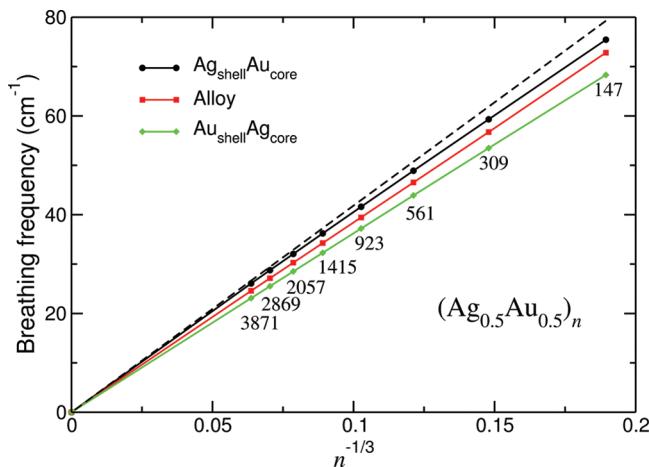
**Published:** March 22, 2012



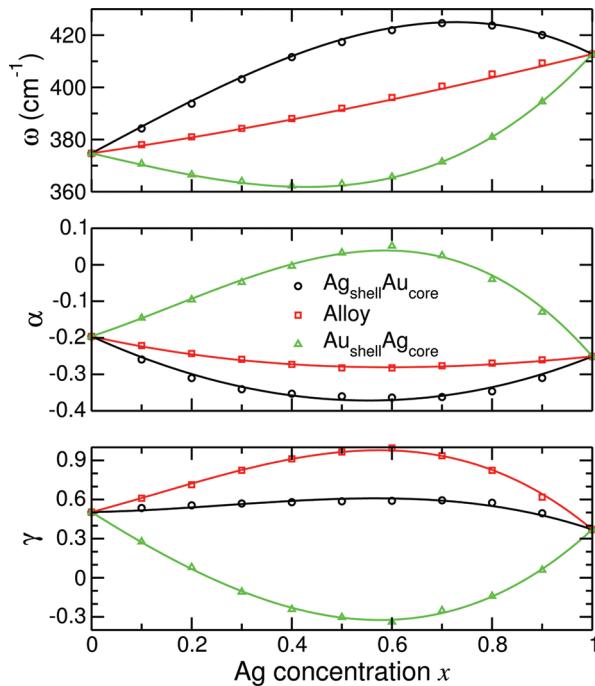
**Figure 3.** (Corrected) Breathing frequency of icosahedral Ag–Au nanoalloys as a function of Ag concentration and for different types of chemical ordering. The results are shown for 561-atom and 923-atom clusters as dashed and solid lines, respectively, and the error bars indicate the standard deviation due to averaging over homotops.



**Figure 4.** (Corrected) Breathing frequency of cuboctahedral, 923-atom Ag–Au nanoalloys as a function of Ag concentration and for different types of chemical ordering. The error bars indicate the standard deviation due to averaging over homotops.



**Figure 5.** (Corrected) Breathing frequency of icosahedral Ag–Au nanoalloys at fixed Ag concentration of 0.5, as a function of  $n^{-1/3} \propto 1/D$ , with  $D$  being the inverse cluster diameter, and for different types of chemical ordering. The dashed straight line shows the perfect  $1/D$  behavior. The individual nanoparticle sizes are also indicated.



**Figure 6.** (Corrected) Leading ( $\omega$ ) and correcting ( $\alpha$  and  $\gamma$ ) terms in the expansion of the breathing frequency versus nanoparticle size, as a function of silver concentration and for different types of chemical ordering. The solid lines are best fit quadratic expansions with fixed end points.

**Table 1. (Corrected) Parameters of the Polynomial Expansion for the Breathing Frequency As a Function of Size  $n$  and Composition  $x$  for Icosahedral (ico) Clusters<sup>a</sup>**

Pure Elements			
	$\omega$	$\alpha$	$\gamma$
Ag(ico)	412.8	-0.251	0.370
Au(ico)	374.7	-0.197	0.504
Ag(cubo)	409.0	-0.282	0.276
Au(cubo)	371.9	-0.221	0.411
Mixed Elements (ico)			
	$\omega_{\text{mix}}$	$\alpha_{\text{mix}}$	$\gamma_{\text{mix}}$
$\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$	59.43	-0.57	0.197
Alloy	-7.75	-0.25	1.15
$\text{Ag}_{\text{core}}\text{Au}_{\text{shell}}$	-42.52	0.51	-2.29
	$\delta\omega_{\text{mix}}$	$\delta\alpha_{\text{mix}}$	$\delta\gamma_{\text{mix}}$
$\text{Ag}_{\text{shell}}\text{Au}_{\text{core}}$	64.2	-0.03	0.953
alloy	24.6	0.058	1.92
$\text{Ag}_{\text{core}}\text{Au}_{\text{shell}}$	-85.7	1.01	-1.36

<sup>a</sup>The contributions from the pure and mixed elements are given also for cuboctahedral (cubo) clusters, with  $\omega$  in wavenumbers and both  $\alpha$  and  $\gamma$  dimensionless.

found. We thus introduce for each of these quantities an alternative two-parameter cubic model as

$$\omega(x) = x\omega_{\text{Ag}} + (1-x)\omega_{\text{Au}} + x(1-x)\omega_{\text{mix}} + x^2(1-x)\delta\omega_{\text{mix}} \quad (2)$$

where  $\omega_{\text{Ag}}$  and  $\omega_{\text{Au}}$  are the values for the pure metals; and  $\omega_{\text{mix}}$  and  $\delta\omega_{\text{mix}}$  are two mixing parameters of first and second order. Similar forms are used for  $\alpha(x)$  and  $\gamma(x)$ . The parameters obtained by fitting the computed breathing frequencies using these models

are all given in Table 1. The values of  $\omega$  for pure gold and silver were previously off by  $-15$  and  $+165\text{ cm}^{-1}$  with respect to experiment, respectively. The new extrapolation changes these discrepancies to  $+55$  and  $+72\text{ cm}^{-1}$ , respectively, indicating some improvement. If cuboctahedra are considered instead of icosahedra, then the extrapolation to the bulk face-centered cubic structure is also better and the agreement with the experimental frequencies further improves.

## ■ ACKNOWLEDGMENTS

The author wishes to thank Prof. I. L. Garzón for useful discussions that lead to detecting the inconsistencies in the original paper.

## ■ REFERENCES

- (1) Calvo, F. *J. Phys. Chem. C* **2011**, *115*, 17730.