Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Vibrational Properties and Specific Heat of Core-Shell Ag-Au Icosahedral Nanoparticles

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Part I. Parameters of the Many-Body Gupta Potential.

To model the metallic bonding in the systems under study the *n*-body Gupta potential was used. Such potential for a bimetallic system is given by:

$$U(\{r_k\}) = \sum_{i=1}^{N} U_i = \sum_{i=1}^{N} \left\{ \sum_{j\neq i}^{N} \epsilon_{ij} e^{-p_{ij}\left(r_{ij}/r_{ij}^0 - 1\right)} - \left[\sum_{j\neq i}^{N} \zeta_{ij}^2 e^{-2q\left(r_{ij}/r_{ij}^0 - 1\right)} \right]^{1/2} \right\}$$

The parameters $\epsilon_{ij}, \zeta_{ij}, p_{ij}, q_{ij}$ and r_{ij}^0 are fitted to bulk material properties. In this paper, a set of parameters fitted by Cleri and Rosato[1] were used in the case of homoatomic interactions, while for Au-Ag interactions, a combination of geometrical and arithmetical averages of the pure metal parameters were used. These parameters are shown in Table S1.

There is another set of parameters recently used by Calvo[2,3] to compute the frequencies of metal nanoalloys. This second set of parameters were obtained by

Rapallo *et al.*[4] for the Au-Au interaction and in the case of the Ag-Ag one, the parameters were fitted by Baletto *et al.*[5] For the Au-Ag interaction, the parameters were fitted by Rapallo *et al.*[4] to the solubility energies in the case of ϵ_{ij} and ζ_{ij}, and for the p_{ij} and q_{ij}, an arithmetic average of the pure values was caried out.

Table S1. Parameters of the Gupta potential. The parameters used in this work are the values fitted by Cleri and Rosato[1] and their geometric and arithmetic averages for the heteroatomic interaction. Other parameter values were obtained by Rapallo et al. (Au-Au),[4] Baletto et al. (Ag-Ag)[5], and Rapallo et al. (Au-Ag).[4]

Material	ϵ_{ij} [eV]	ζ_{ij} [eV]	p_{ij}	q_{ij}	r_{ij}^{0}[Å]	Refs.
Au-Au	0.2061	1.790	10.229	4.036	2.884	1
Ag-Ag	0.1028	1.178	10.928	3.139	2.889	1
Au-Ag	0.1456[a]	1.4521[a]	10.579[b]	3.588[b]	2.8865[c]	This work
Au-Au (in Au-Ag)	0.2096	1.8153	10.139	4.033	2.884	4
Ag-Ag	0.1031	1.1899	10.85	3.18	2.889	5
Au-Ag	0.149	1.4874	10.494[b]	3.607[b]	2.8865[c]	4

[a] $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$ and $\zeta_{AB} = \sqrt{\zeta_A \zeta_B}$.

[b] $p_{AB} = (p_A + p_B)/2$ and $q_{AB} = (q_A + q_B)/2$.

[c] $r_{AB} = (r_A + r_B)/2$.

Part II. Vibrational density of states (VDOS) of bimetallic nanoparticles

Here it is shown the VDOS for 561- (Fig. S1), 309- (Fig. S2) and 147-atoms (Fig. S3) bimetallic nanoparticles.

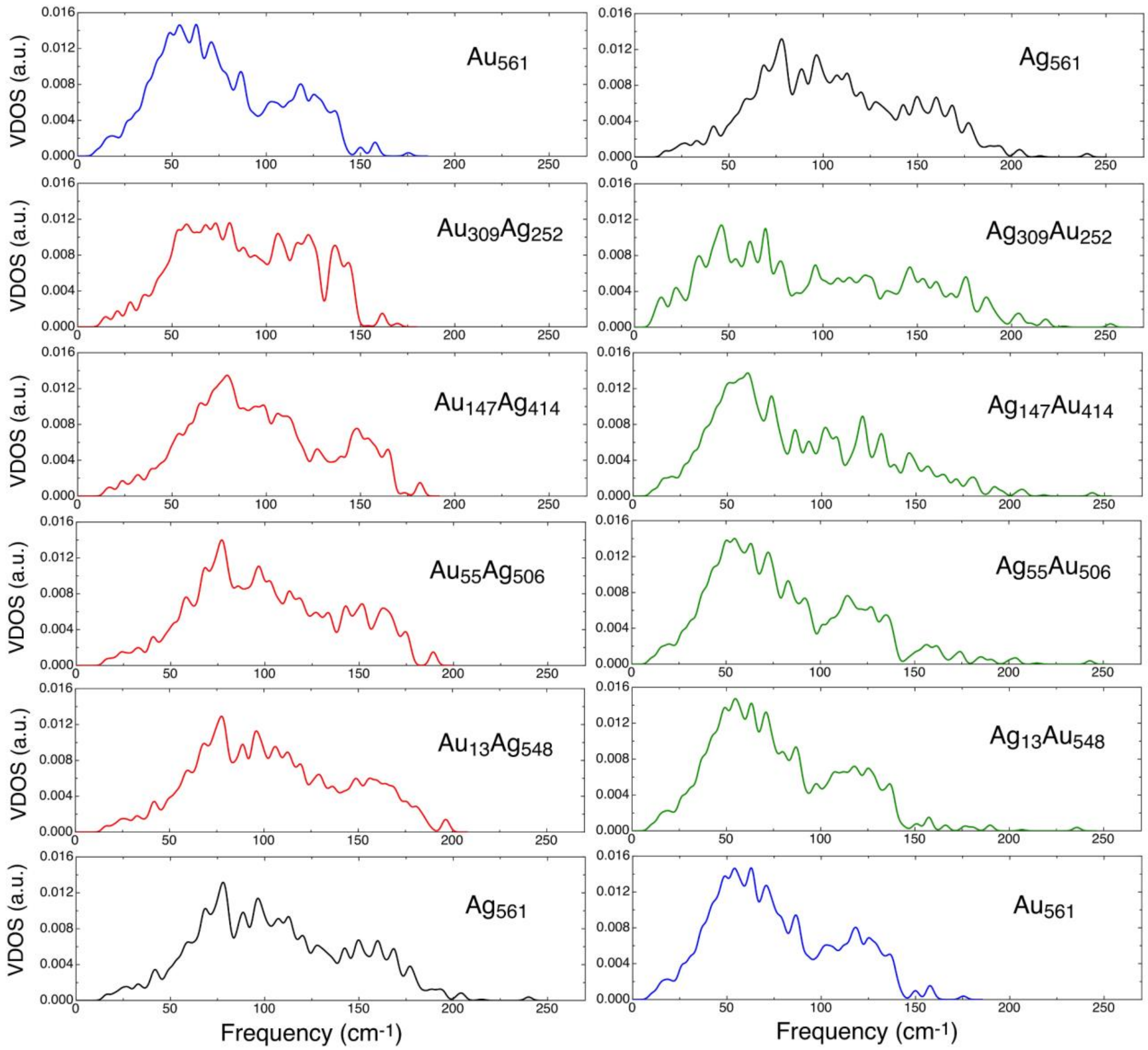

Figure S1. Vibrational density of states (VDOS) for the 561-atom bimetallic icosahedral Au_{core}-Ag_{shell} (left panels) and Ag_{core}-Au_{shell} (right panels) nanoparticles with different core-shell compositions. The VDOS for the pure Au_{561} and Ag_{561} icosahedral nanoparticles are also displayed for comparison.

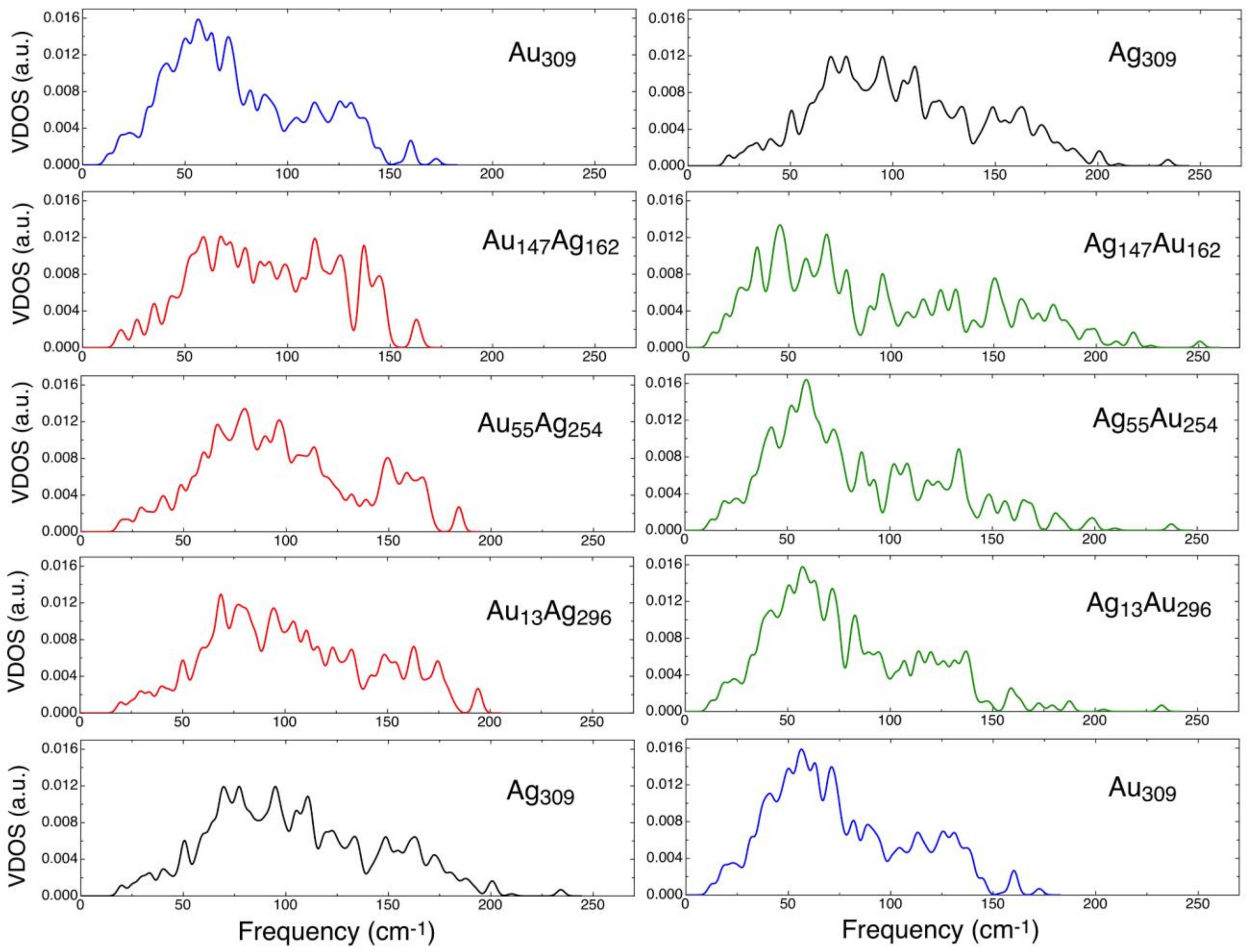

Figure S2. Vibrational density of states (VDOS) for the 309-atom bimetallic icosahedral Au$_{core}$-Ag$_{shell}$ (left panels) and Ag$_{core}$-Au$_{shell}$ (right panels) nanoparticles with different core-shell compositions. The VDOS for the pure Au$_{309}$ and Ag$_{309}$ icosahedral nanoparticles are also displayed for comparison.

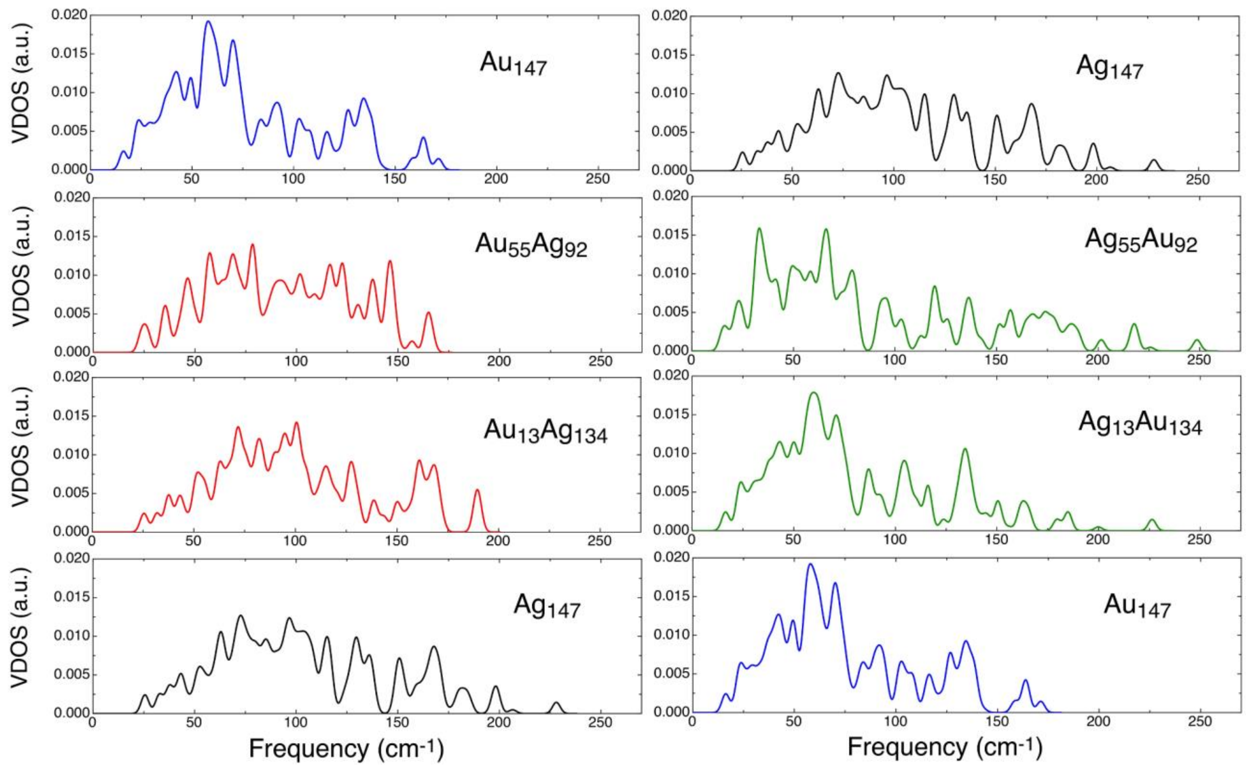

Figure S3. Vibrational density of states (VDOS) for the 147-atom bimetallic icosahedral Au_{core}-Ag_{shell} (left panels) and Ag_{core}-Au_{shell} (right panels) nanoparticles with different core-shell compositions. The VDOS for the pure Au_{147} and Ag_{147} icosahedral nanoparticles are also displayed for comparison.

Part III. Specific heat of bimetallic nanoparticles

The specific heat as a function of temperature is displayed for all 923-atom core-shell Ag-Au icosahedral nanoparticles showed in Fig. 1. The data in Fig. 1 shows a smooth transition between the pure metal nanoparticles. The only case that does not follow this trend is the $Ag_{561}Au_{362}$ nanoparticle with Ag core.

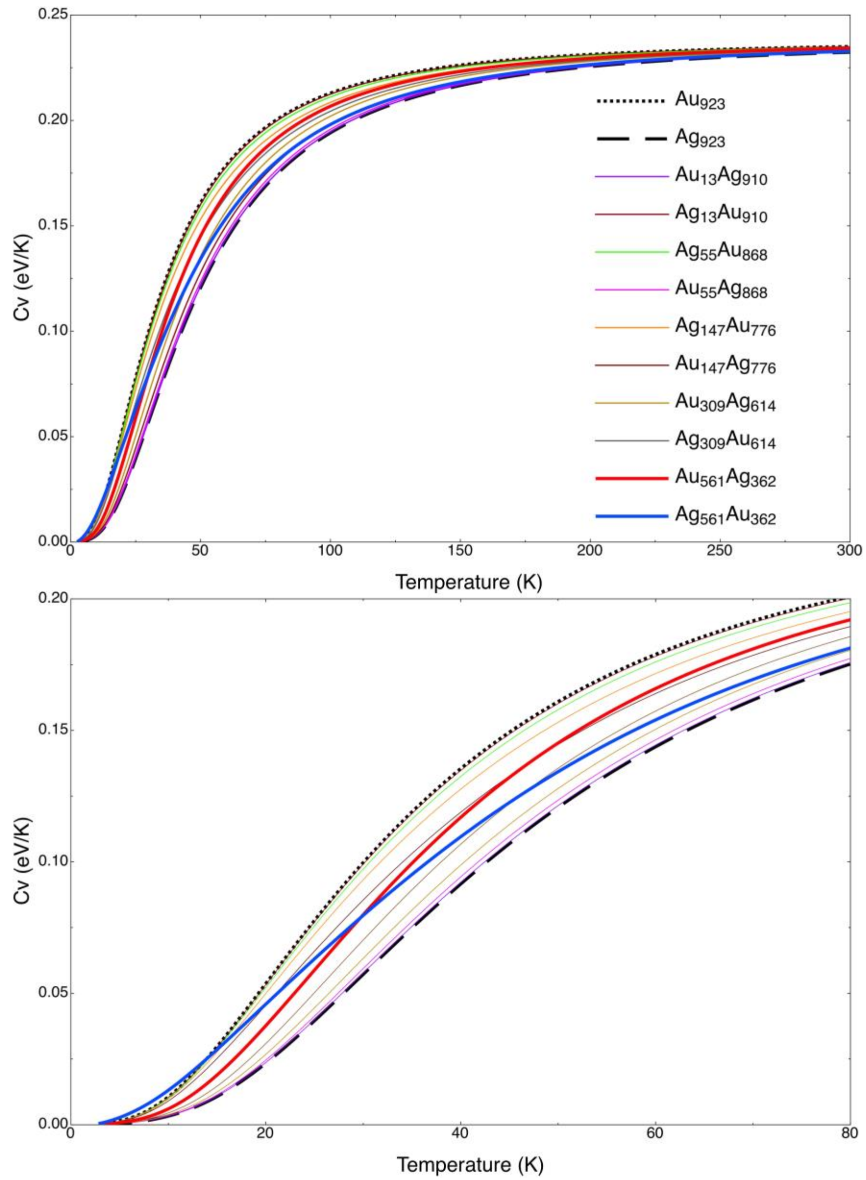

Figure S4. Low-temperature dependence of the specific heat of core-shell bimetallic icosahedral nanoparticles. The bottom panel shows the specific heat in a smaller range of temperature.

References

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