A Water Solvation Shell Can Transform Gold Metastable Nanoparticles In the Fluxional Regime

[Supporting Information]

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1/ Optimized Structures of Free Gold Nanoparticles

In the following section, all the optimal geometries of the free gold nanoparticles have been presented by sorting them according to the 6 explored polyhedral morphologies : truncated octahedron, icosahedron, ino-decahedron, cuboctahedron, regular decahedron and Marks-decahedron (DFT, PBE-D3 level of calculation).

The cohesion energy per Au atom is defined as follows:

$$\Delta E_{coh} = \frac{E_{tot}(AuNP) - N_{Au} * E_{tot}(Au_{iso})}{N_{Au}} \quad \text{[Eq. S1]}$$

where N_Au is the total number of Au atoms in Au NP, $E_{tot}(AuNP)$being the total electronic energy of the relaxed nanocluster and $E_{tot}(Au_{iso})$being the total electronic energy of an isolated gold atom. This theoretical descriptor is used in Figure 2 of the article.

The excess energy per atom is an alternative theoretical descriptor corresponding to the Au NP stability, of which the usual formula is the following one :

$$\Delta E_{exc} = \frac{E_{tot}(AuNP) - N_{Au} * E_{tot}(Au_{bulk})}{N^{2/3}} \quad \text{[Eq. S2]}$$

where $E_{tot}(AuNP)$ is the total electronic energy of the Au NP and $E_{tot}(Au_{bulk})$ being the total electronic energy of gold bulk (1 atom in the primitive cell). The energetic balance between the Au NP and the bulk is similar to a surface energy. $N^{2/3}$ is the normalization constant chosen empirically to take into account the proportion of surface Au atoms with respect to the core Au atoms. This theoretical descriptor is used in Figure 2 of the article.

1.1/ Truncated Octahedral Nanoclusters

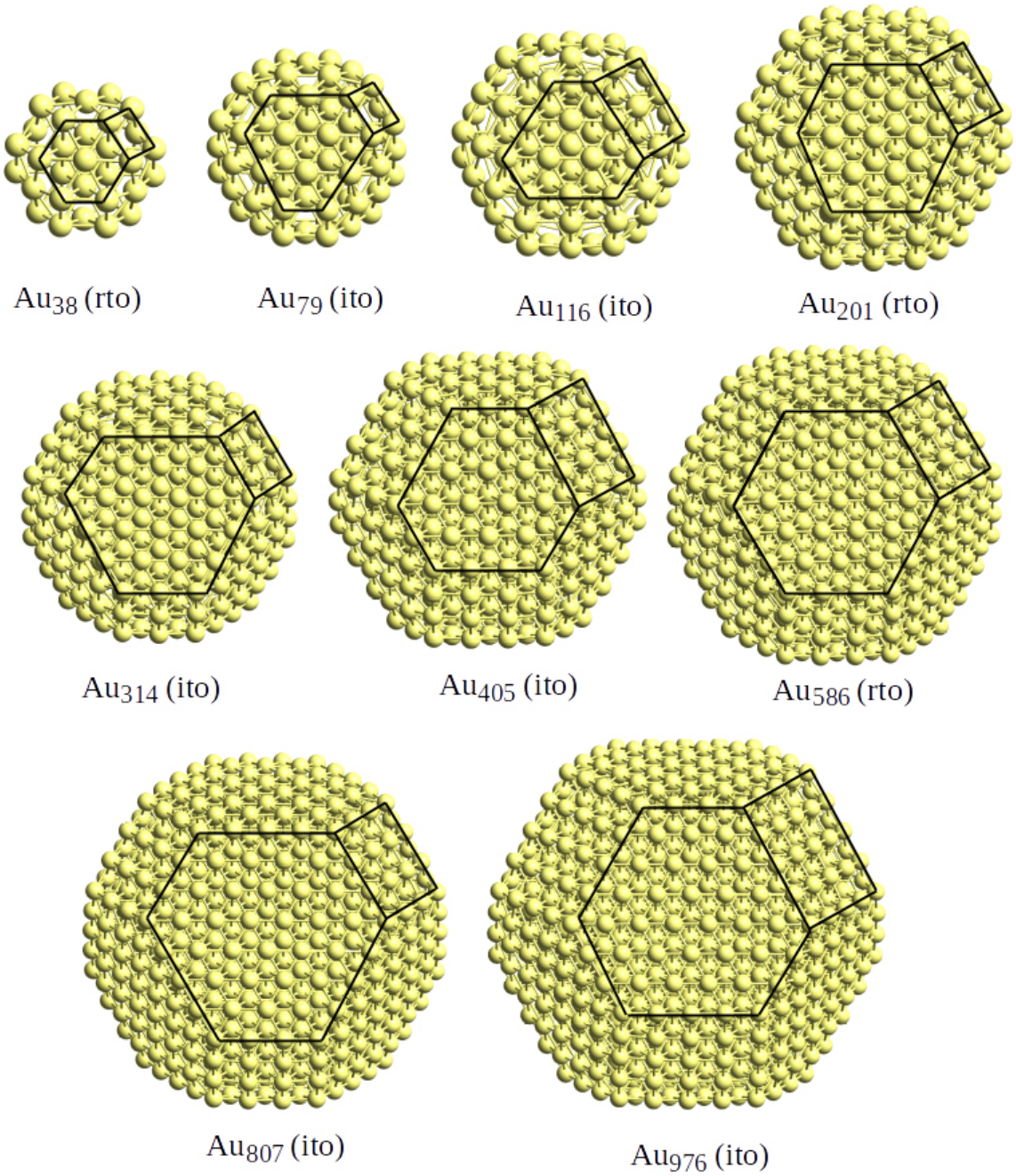

Figure S1. Optimized structures of regular (rto) and irregular (ito) truncated octahedral Au NPs in the range 0.9-3.4 nm.

1.2/ Icosahedral Nanoclusters

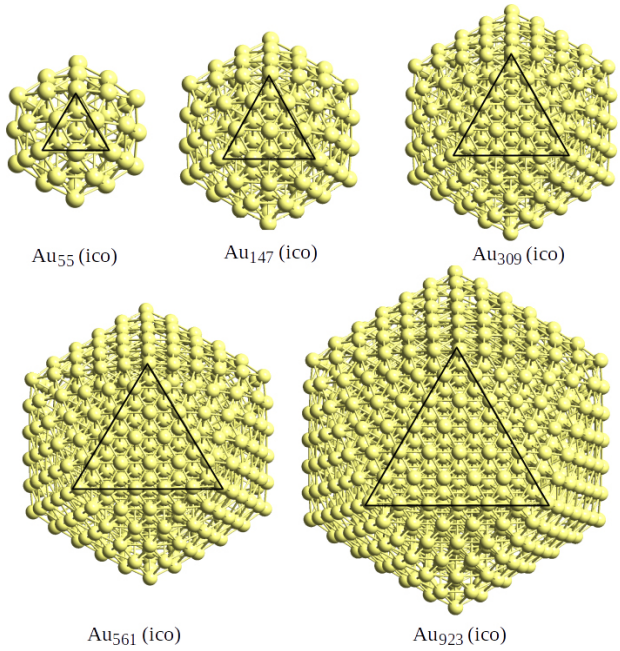

Figure S2. Optimized structures of icosahedral Au NPs in the range 0.9-3.4 nm.

1.3/ Ino-decahedral Nanoclusters

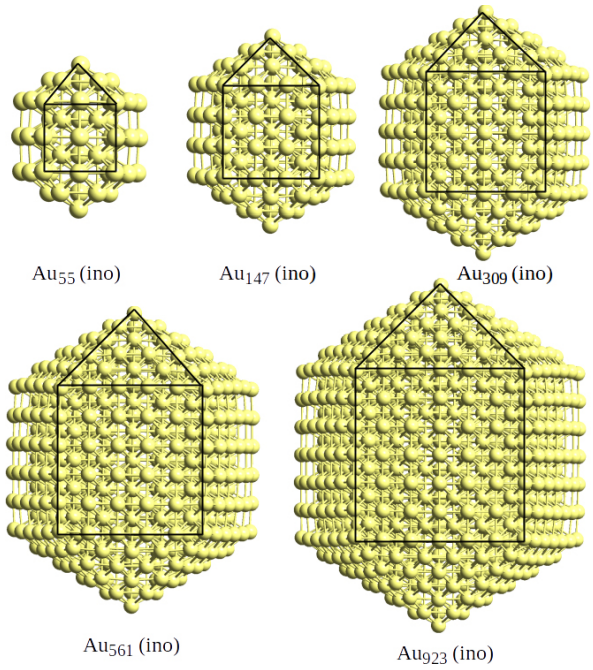

Figure S3. Optimized structures of ino-decahedral Au NPs in the range 0.9-3.4 nm.

1.4/ Cuboctahedral Nanoclusters

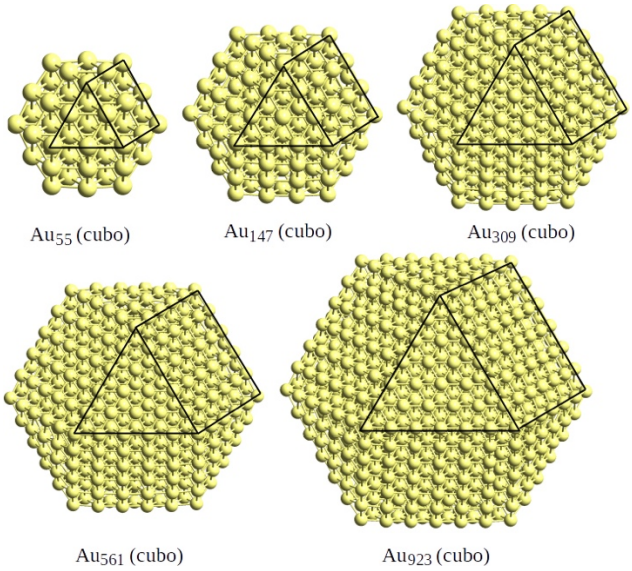

Figure S4. Optimized structures of cuboctahedral Au NPs in the range 0.9-3.4 nm.

1.5/ Regular Decahedral Nanoclusters

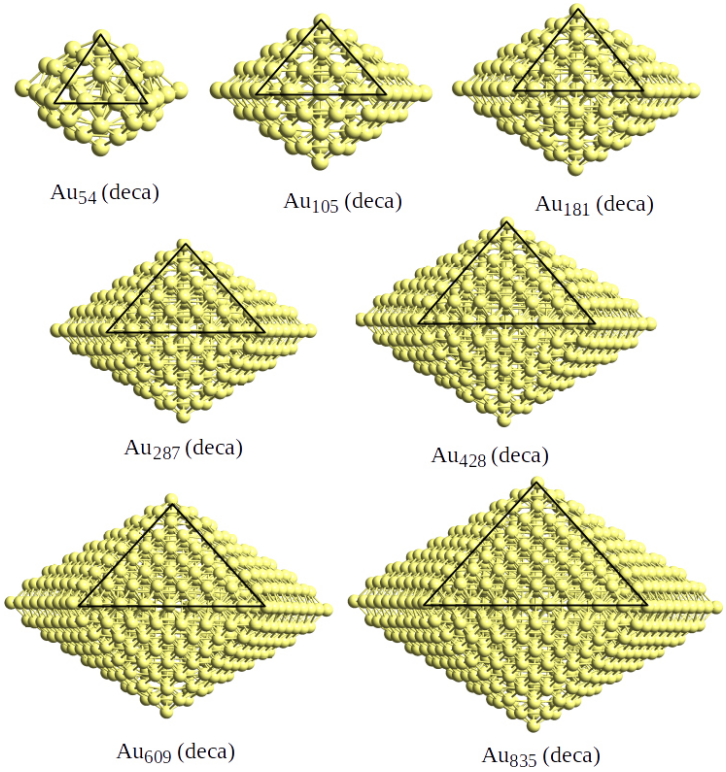

Figure S5. Optimized structures of regular decahedral Au NPs in the range 0.9-3.4 nm.

1.6/ Marks-decahedral Nanoclusters

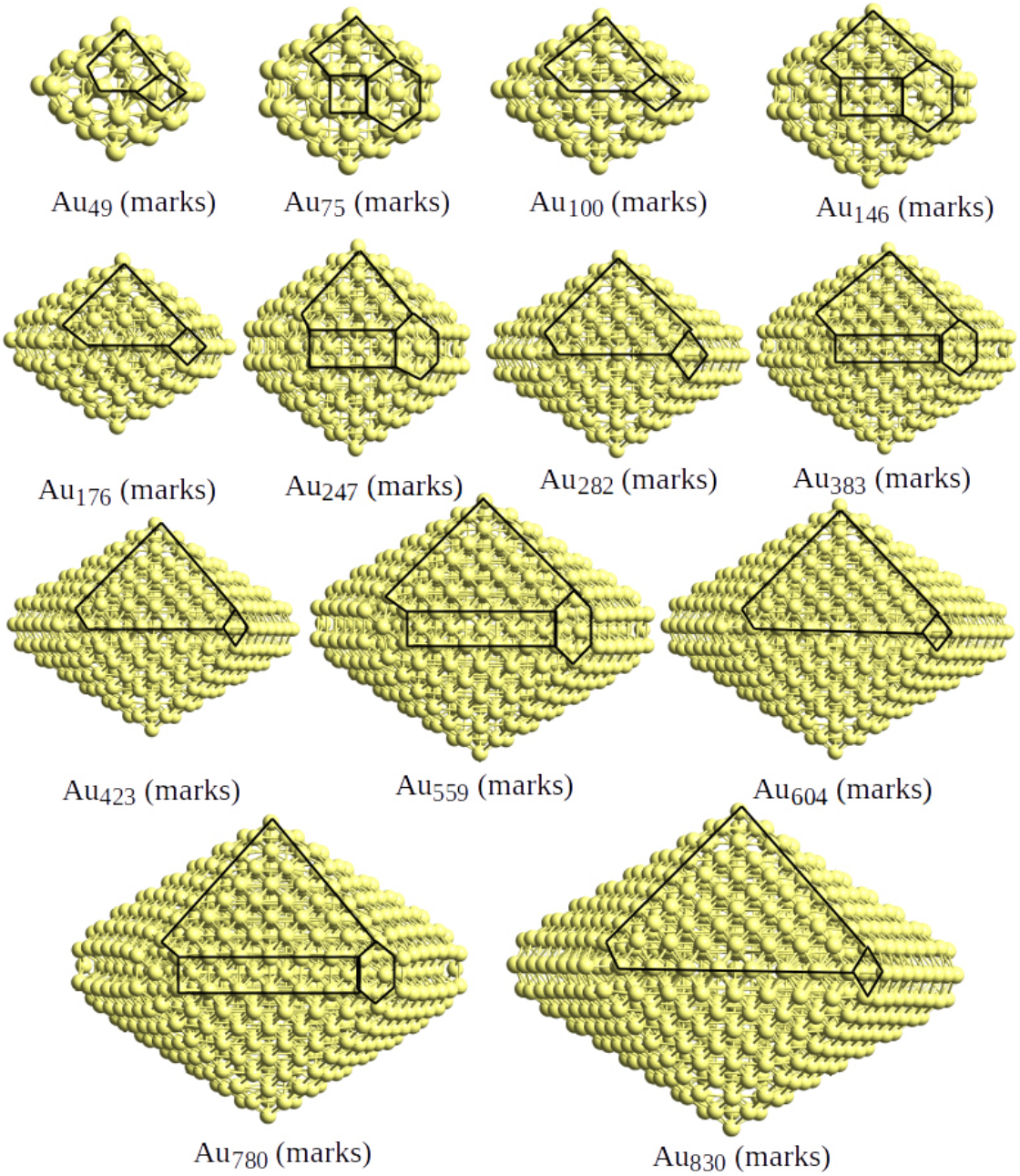

Figure S6. Optimized structures of Marks-decahedral Au NPs in the range 0.9-3.4 nm.

2/ Optimized Structures of Adsorbed Water Monomers Against Nanoparticle Size and Shape

In the following section, all the adsorption properties of water monomers on 9 different Au nanoclusters have been exposed : optimal geometries, adsorption site, adsorption energies (eV)

and Au-O distance (Å) (DFT PBE-D3 level of calculation). For Au_{38} (rto), all the possible top, bridge and fcc and hcp threefold hollow sites have been considered (considering the non-equivalent positions depending on their location : corners, edges and (111) or (100) facets). After the geometry optimizations, the bridge and hollow adsorption forms have all diffused to top positions. Hence, since these two latter sites have been found unstable, in the following the optimal top adsorption structures will be presented for all the Au nanoclusters.

The adsorption energy of one water monomer on the various Au NPs is expressed as follows:

$$\Delta E_{ads} = E_{tot}(AuNP - H_2O) - E_{tot}(AuNP) - E_{tot}(H_2O) \text{ [Eq. S3]}$$

where $E_{tot}(AuNP - H_2O)$ is the total electronic energy of the complete relaxed system (water monomer adsorbed on the Au NP), $E_{tot}(AuNP)$ being the total electronic energy of the isolated relaxed AuNP (with a starting guess for the geometry optimization being the deformed Au structure in presence of water) and $E_{tot}(H_2O)$ being the total electronic energy of the isolated relaxed water molecule.

2.1/ Regular Truncated Octahedral Au_{38} Nanocluster

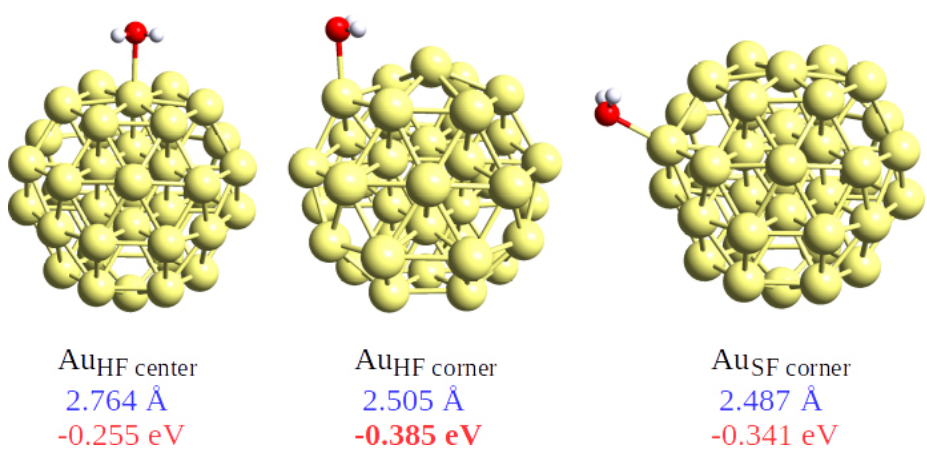

Figure S7. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{38} (rto). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.2/ Regular Decahedral Au_{54} Nanocluster

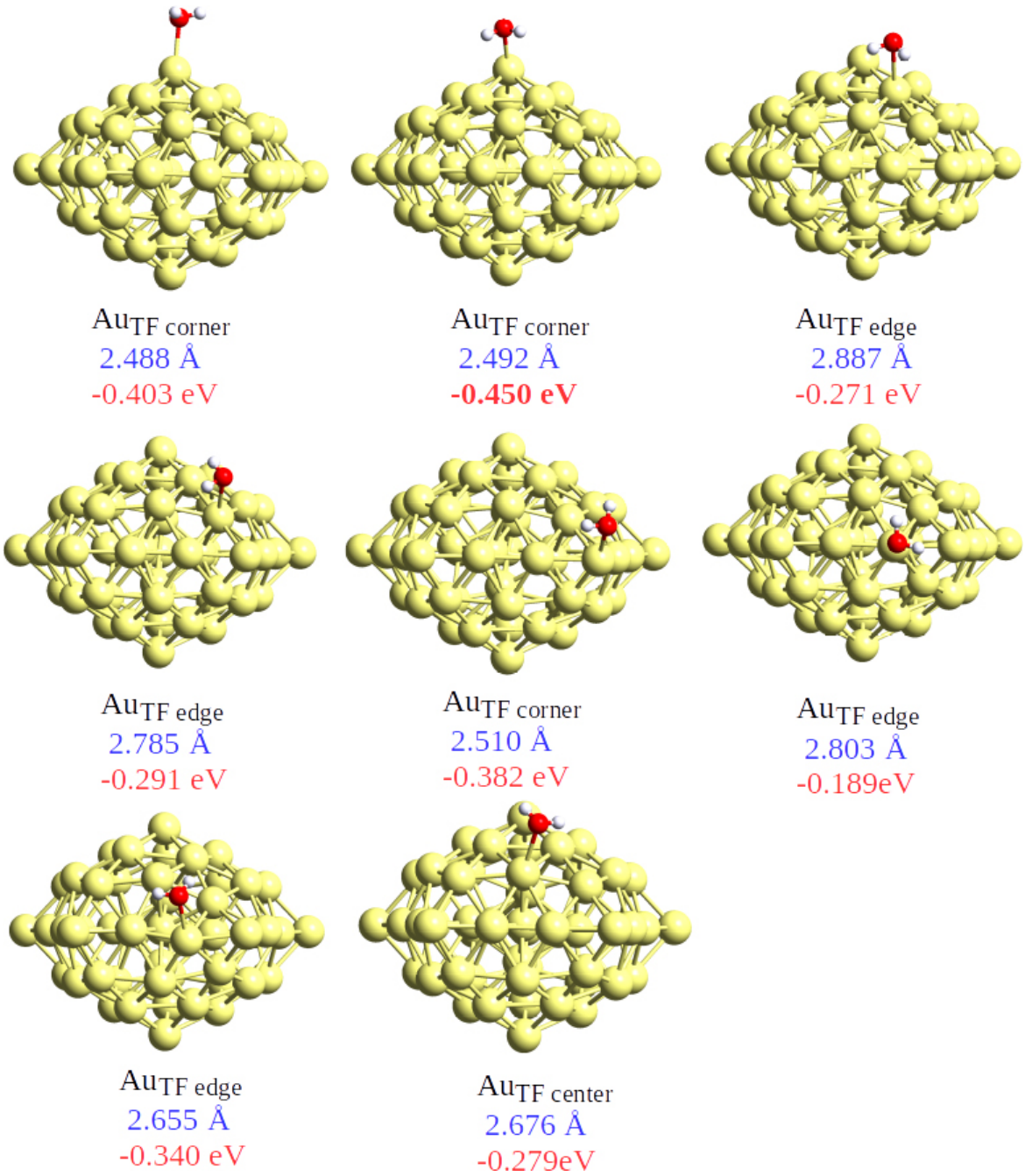

Figure S8. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{54} (deca). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.3/ Icosahedral Au_{55} Nanocluster

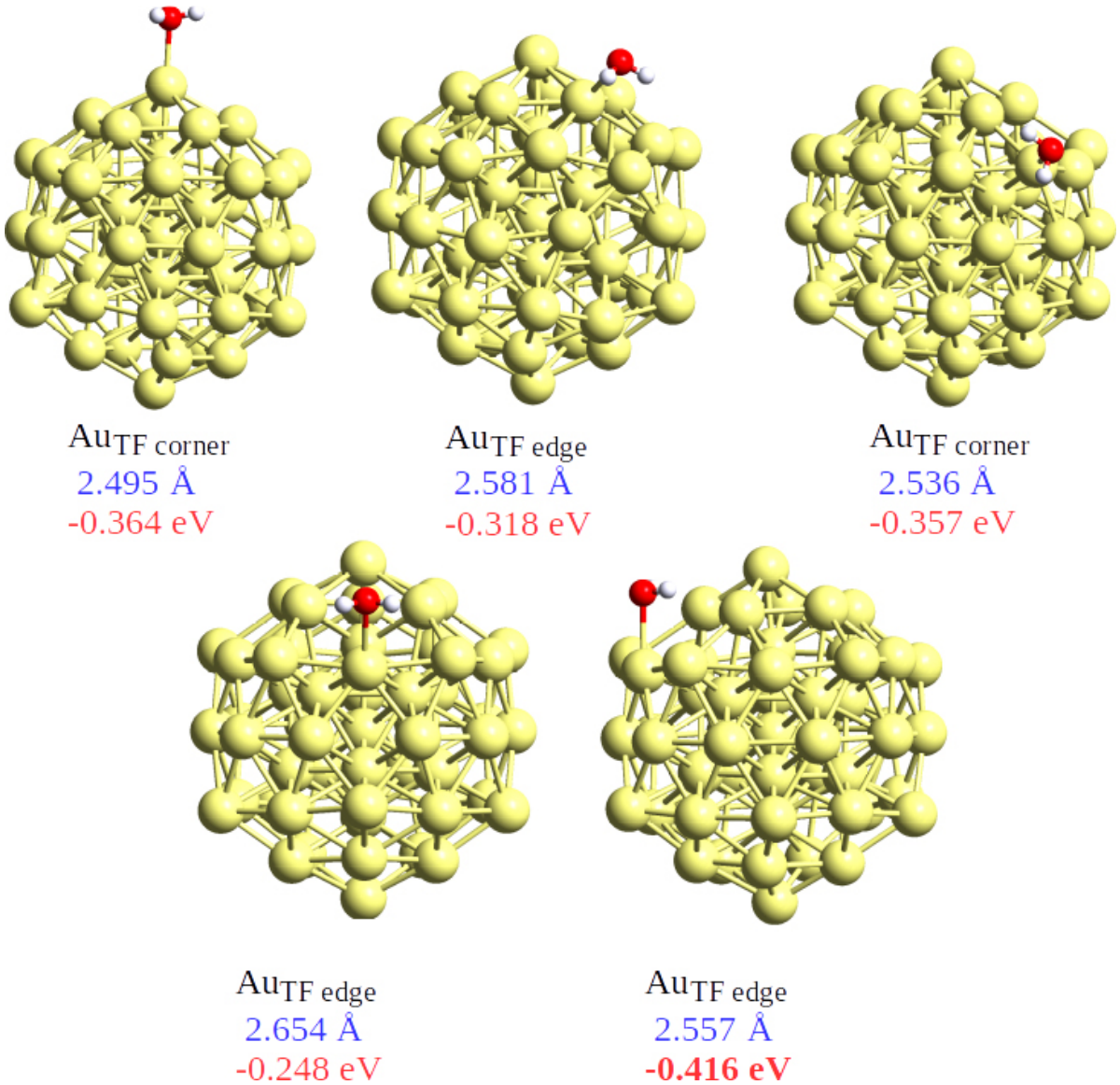

Figure S9. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{55} (ico). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.4/ Ino-decahedral Au_{55} Nanocluster

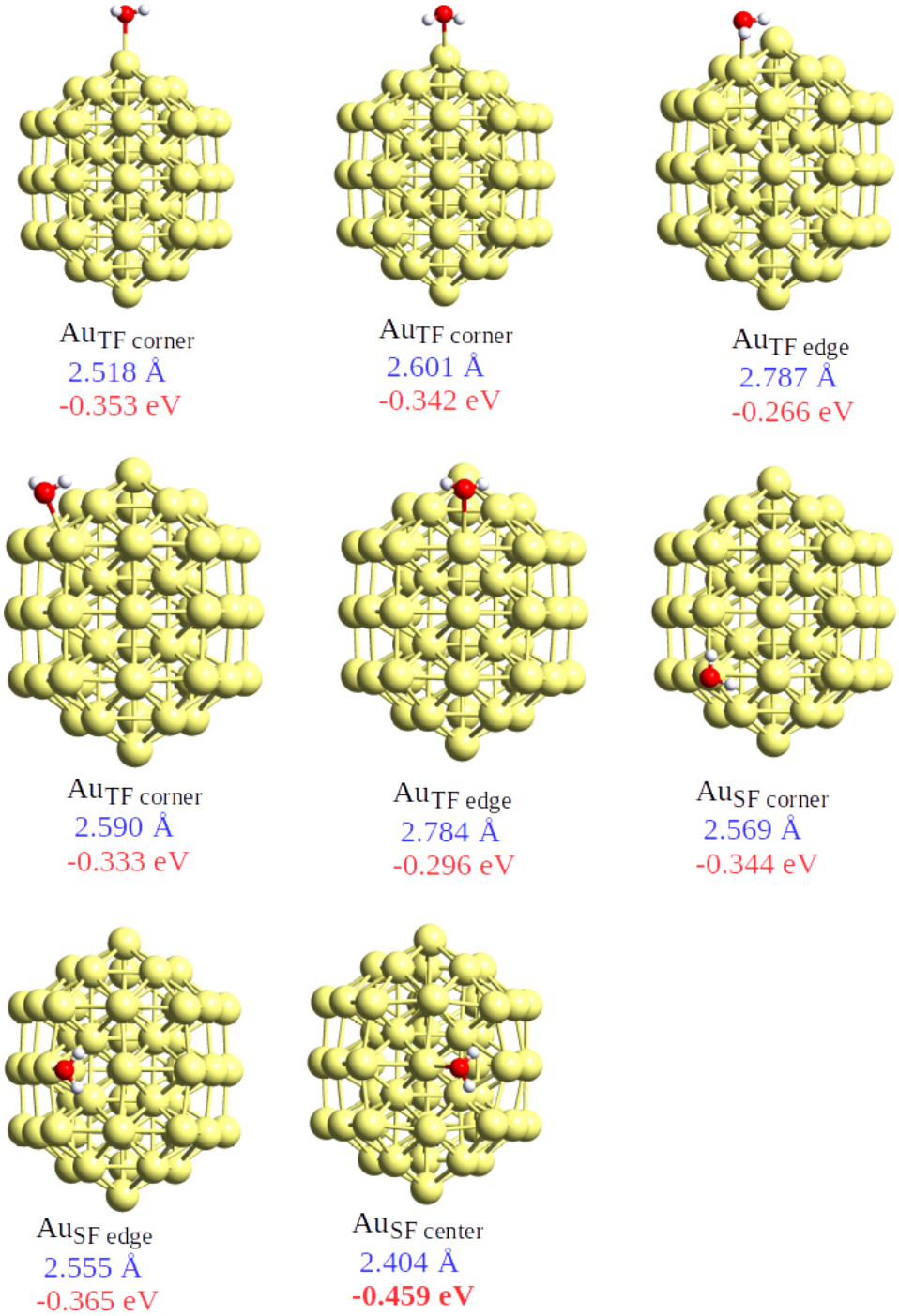

Figure S10. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{55} (ino). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.5/ Irregular Truncated Octahedral Au_{79} Nanocluster

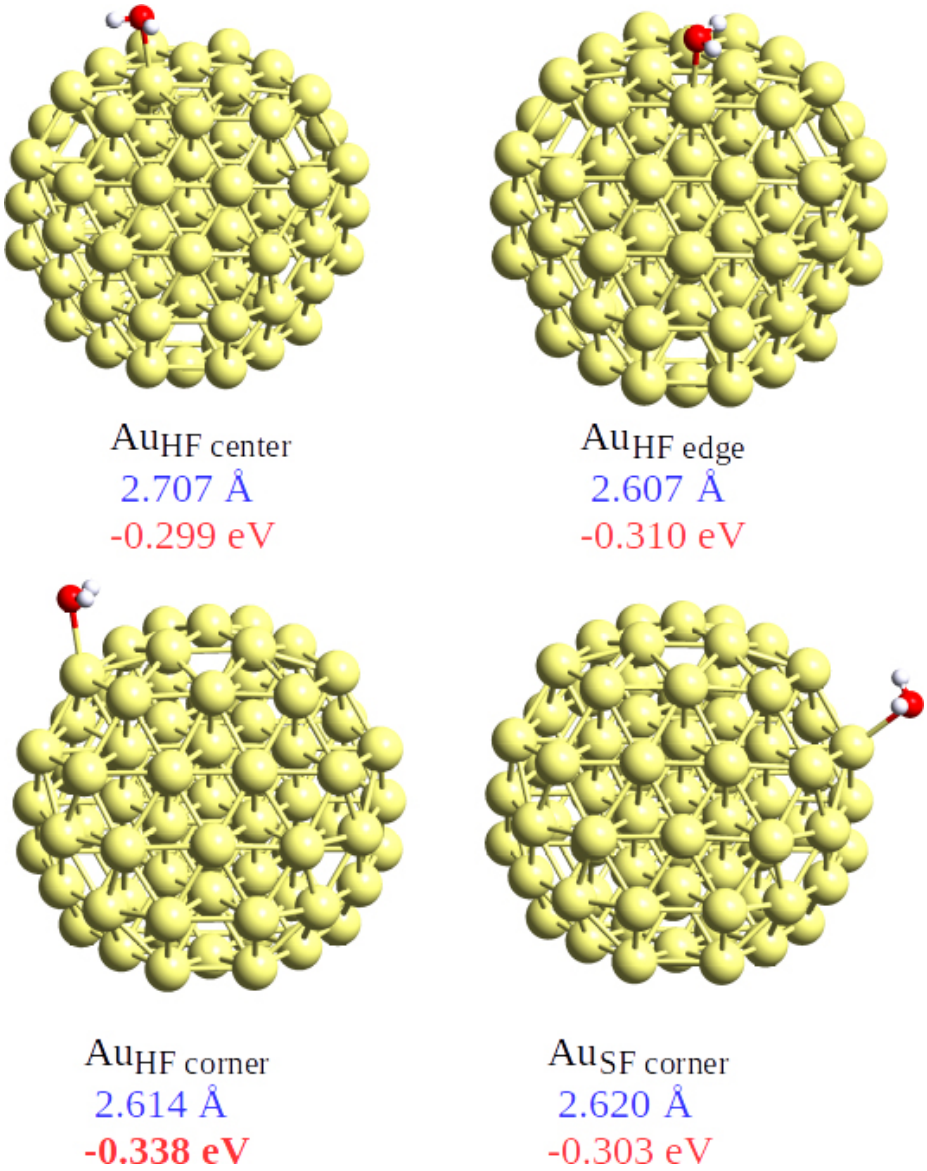

Figure S11. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{79} (ito). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.6/ Regular Decahedral Au_{105} Nanocluster

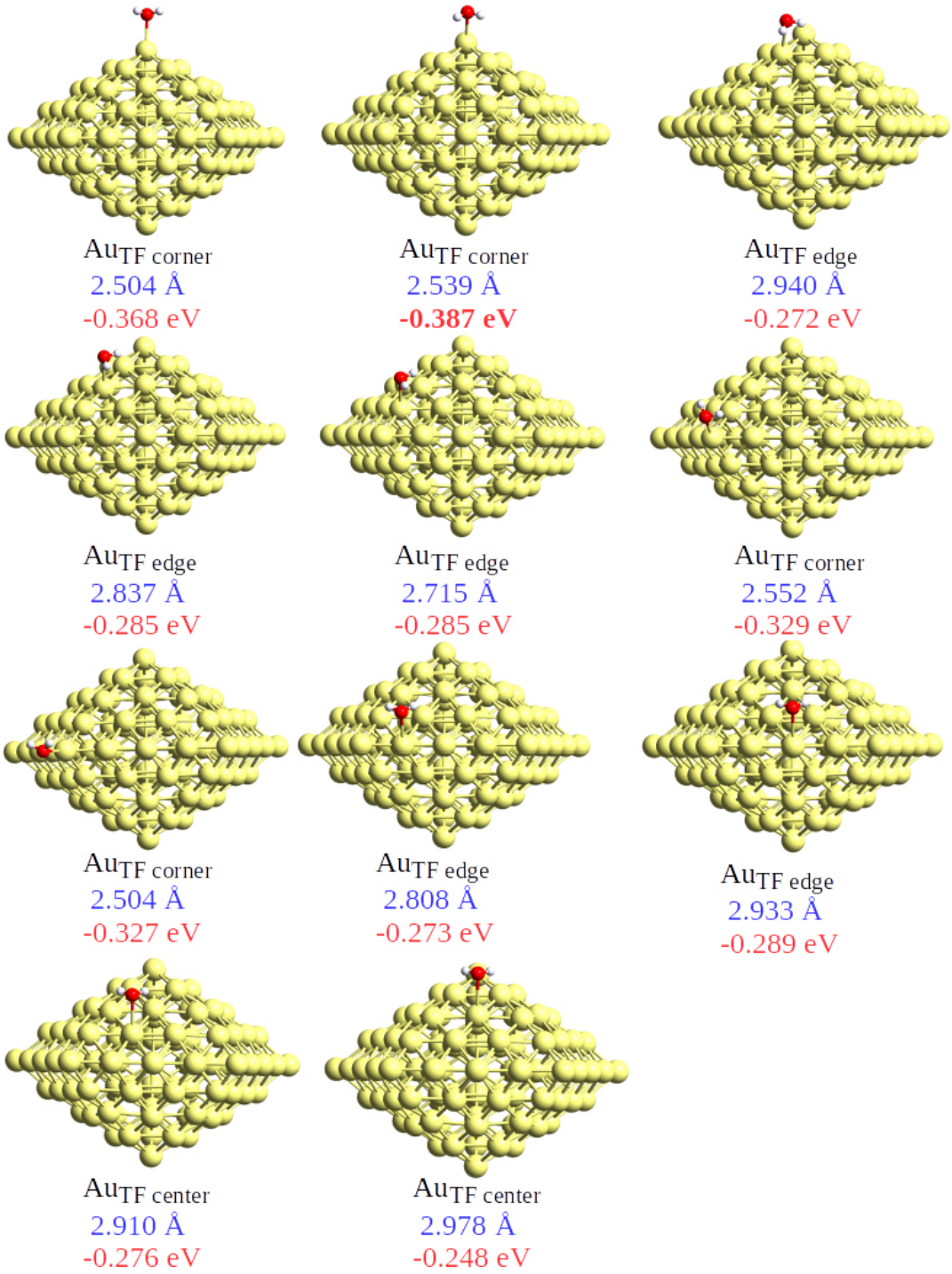

Figure S12. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{105} (deca). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.7/ Icosahedral Au_{147} Nanocluster

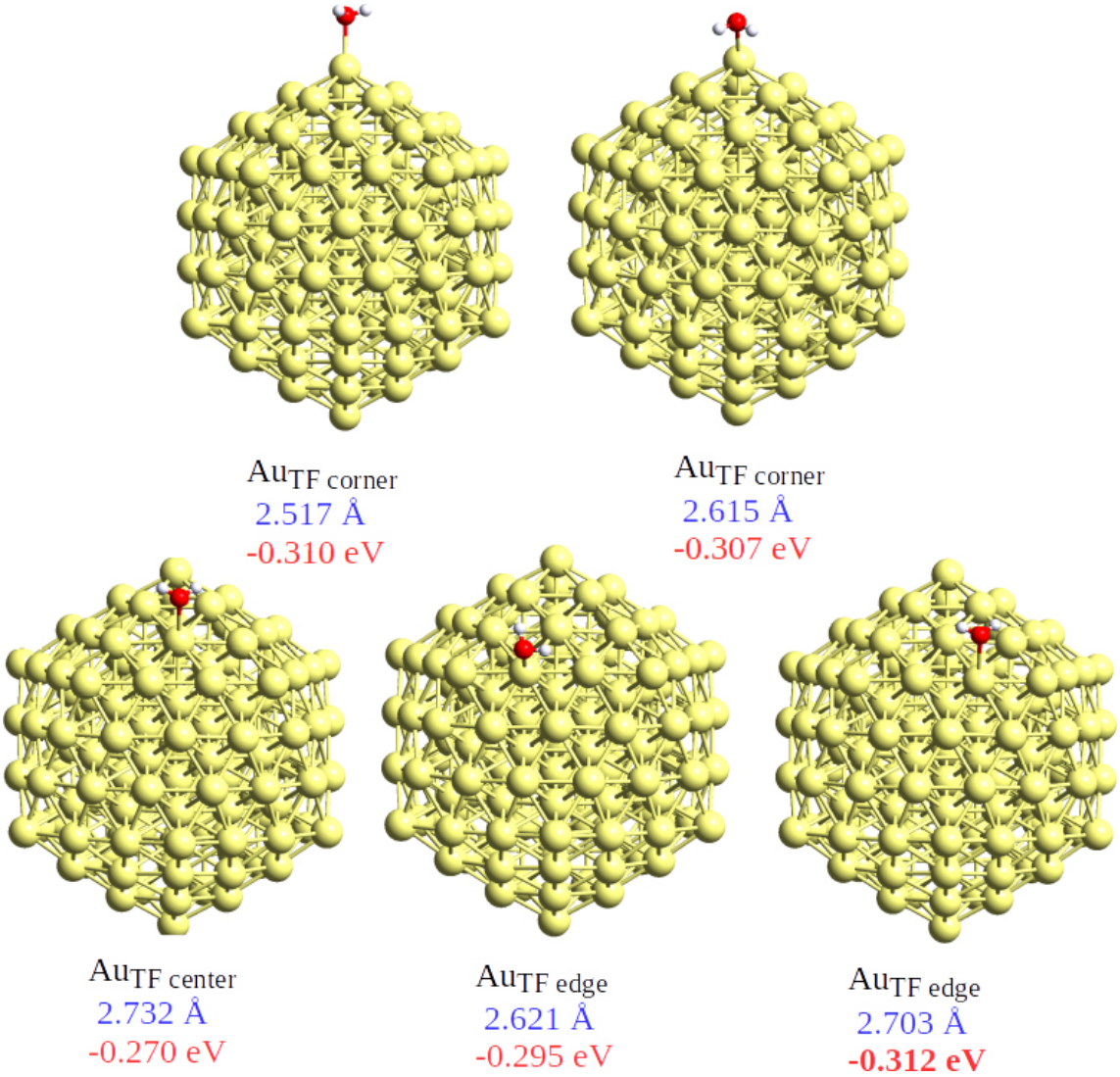

Figure S13. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{147} (ico). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.8/ Ino-decahedral Au_{147} Nanocluster

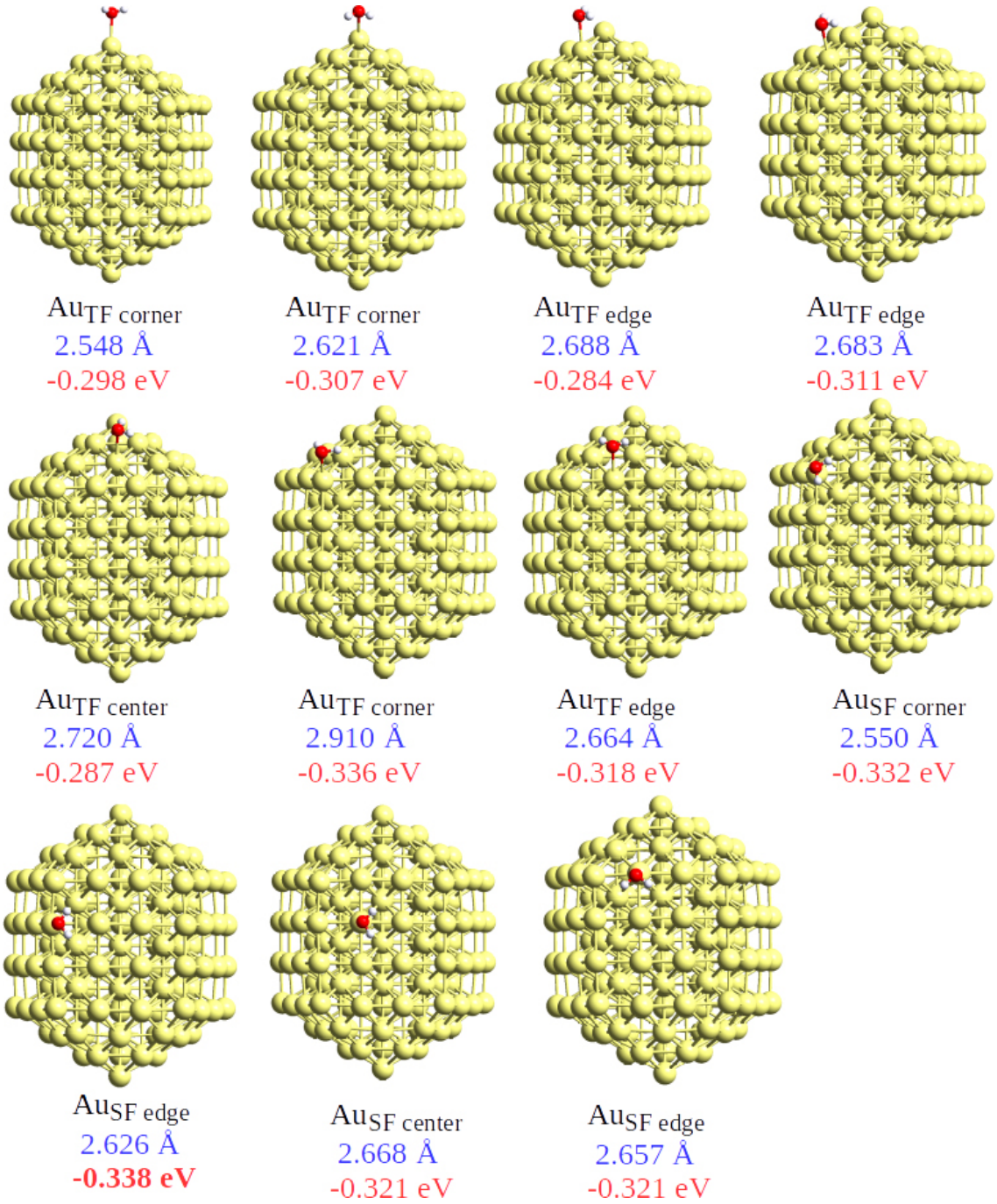

Figure S14. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{147} (ino). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.9/ Regular Truncated Octahedral Au_{201} Nanocluster

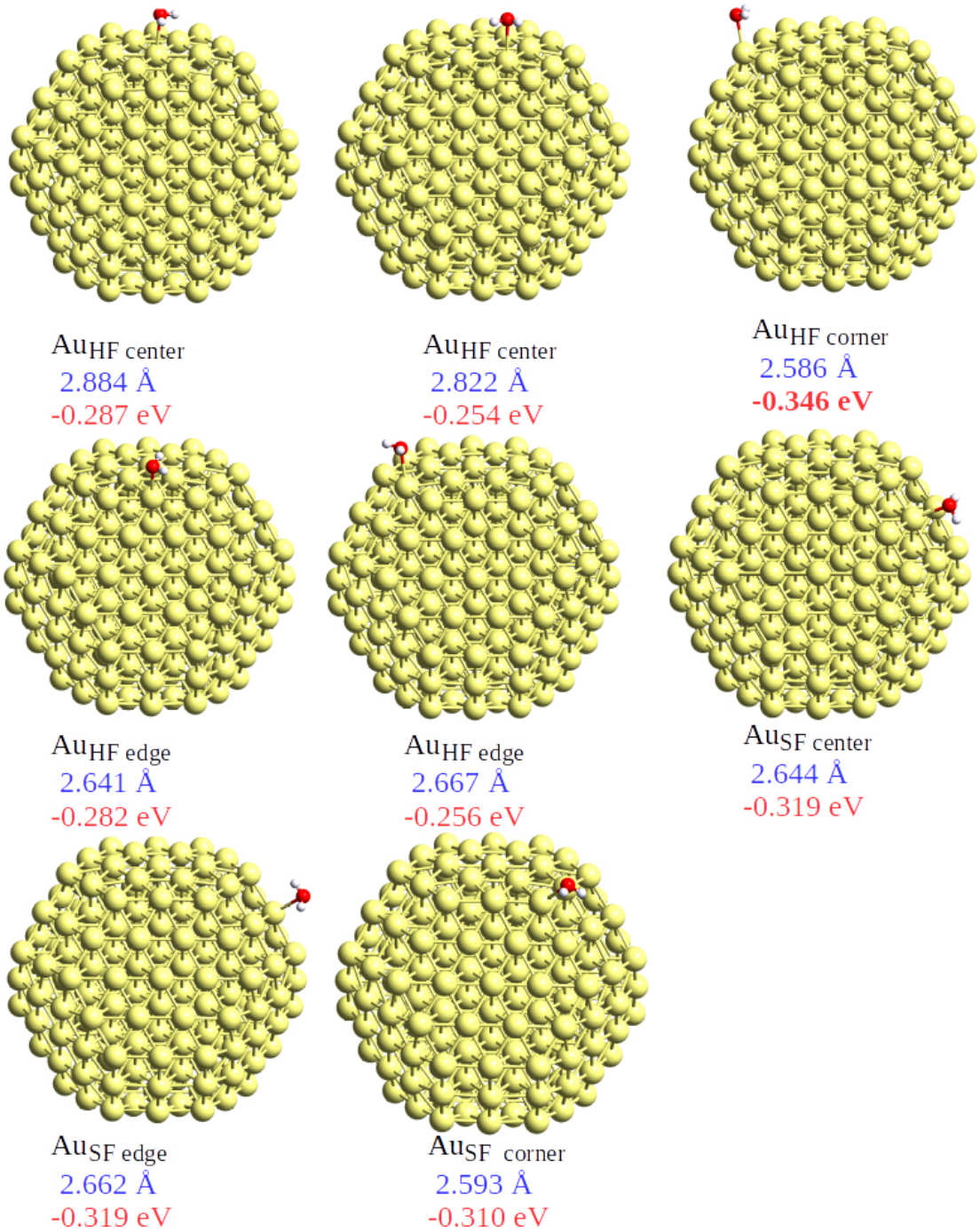

Figure S15. Optimized adsorption structures of water monomers on different top adsorption sites for Au_{201} (rto). The Au-O bond distances are reported in blue characters (Å), whereas the adsorption energies in red characters (eV). The adsorption energy of the most stable site is bolded.

2.10/ Adsorption Energy for Water Monomer : Covalence and Dispersion Contributions

In this section, the adsorption energy ΔE_{ads} (eV) of each water monomer on the 9 different Au nanoclusters (0.9-1.8 nm) has been decomposed into two contributions : pure DFT GGA PBE term, noted ΔE_{cov} (eV) and dispersion D3 semi-empirical corrective term, named ΔE_{disp} (eV).

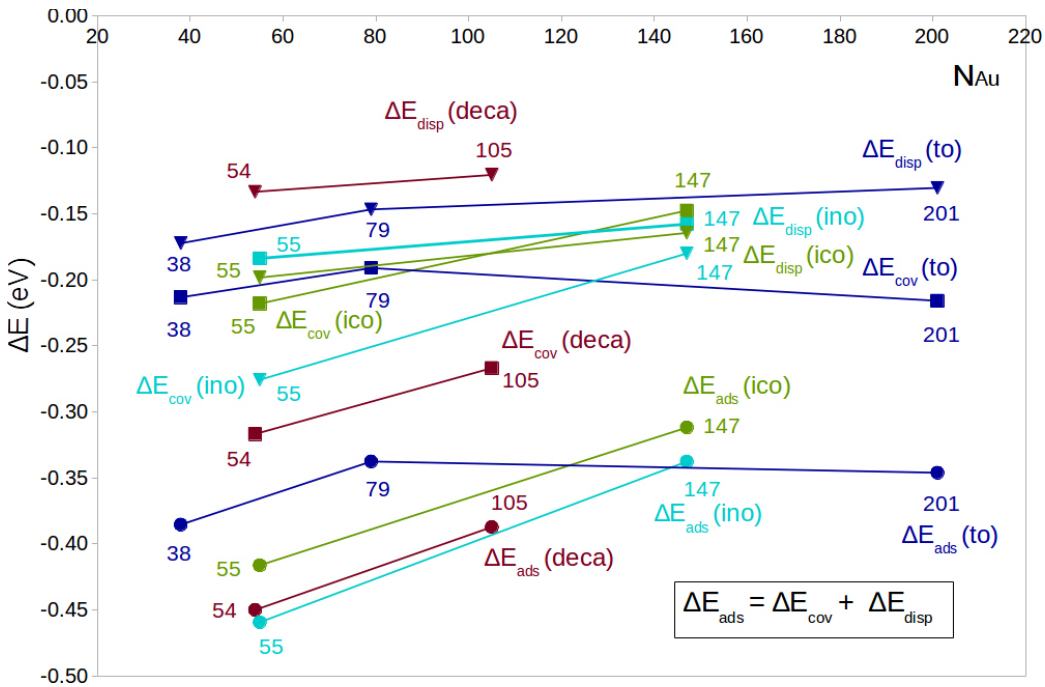

Figure S16. Energy decomposition analysis (EDA) of adsorption energy ΔE_{ads} for water monomers on Au NPs. ΔE_{ads} (points in circle) is defined as the sum of pure GGA PBE ("covalence") energy ΔE_{cov} (points in square) and dispersion energy ΔE_{disp} (points in triangle). These energies for truncated octahedral, icosahedra, ino-decahedra and decahedra are differentiated by blue, green, cyan, and brown color, respectively.

As a preliminary remark, in the decomposition energy model, the two components are systematically negative and thus stabilizing. They are equivalent in proportion in the range 30-60% for dispersion and 40-70% for the pure GGA PBE term ("covalence"). Both of them globally capture the trends of the adsorption energy.

3/ Water Monoshells Adsorbed on Au NPs

In the following section, all the adsorption properties of water monoshells on 9 different Au nanoclusters have been exposed : number of water molecules (chemisorbed and physisorbed), adsorption energetics and hydrogen bonding (DFT PBE-D3 level of calculation).

The normalized adsorption energy per water molecule in the monoshell is defined as follows:

$$\Delta E_{ads} = \frac{E_{tot}(AuNP-NH_2O)-E_{tot}(AuNP)-NH_2O*E_{tot}(H_2O)}{N_{H2O}} \text{ [Eq. S4]}$$

where $E_{tot}(AuNP - NH_2O)$ is the total electronic energy of the complete relaxed system (water monoshell adsorbed on the Au NP), $E_{tot}(AuNP)$ being the total electronic energy of the isolated relaxed AuNP (with a starting guess for the geometry optimization being the deformed Au structure in presence of water) and $E_{tot}(H_2O)$being the total electronic energy of the isolated relaxed water molecule. N_{H2O} is the total number of water molecules in the monoshells.

3.1/ Adsorption Energy : Covalence and Dispersion Normalized Contributions

As explained in the article, for the water monoshells on the various Au nanoclusters, the adsorption energy normalized per water molecule does not vary with the size and shape of the nanoparticle in the range 0.9-1.8 nm. In contrast with the results exposed in Figure S16 for the adsorption of water monomers, the pure GGA PBE term ("covalence") is always majority (from -0.455 to -0.489 eV): the dispersion term being almost 3 times smaller in amplitude (from -0.150 to -0.165 eV). According to the optimal structures of these water monoshells (see Figure 5 of the article), the "covalence" term corresponds to the chemical bonding between water molecules and Au NPs (chemisorption and physisorption) and to the formed hydrogen bonds between water molecules.

Nanocluster	ΔE_{ads} (eV/H_2O)	ΔE_{cov} (eV/H_2O)	ΔE_{disp} (eV/H_2O)
Au_{38} (rto)	-0.608	-0.458	-0.150
Au_{54} (deca)	-0.639	-0.489	-0.150
Au_{55} (ico)	-0.611	-0.460	-0.151
Au_{55} (ino)	-0.607	-0.455	-0.153
Au_{79} (ito)	-0.632	-0.476	-0.156
Au_{105} (deca)	-0.623	-0.464	-0.159
Au_{147} (ino)	-0.643	-0.483	-0.160
Au_{147} (ico)	-0.627	-0.462	-0.165
Au_{201} (rto)	-0.642	-0.479	-0.163

Table S1. Energetics of water monoshells solvating 9 different Au nanoclusters in the range 0.9-1.8 nm. Decomposition of normalized adsorption energy per water molecule into pure GGE PBE ("covalence") and dispersion contributions.

3.2/ Nanoparticle Structure : Induced Deformation by Water Monoshells

In order to evaluate the influence of the water monoshells on the structure of the Au nanoparticles, we introduce the roundness degree S of the nanocluster as follows :

$$S = \frac{R^{min}}{R^{max}} \text{ [Eq. S5]}$$

where R^{min} (and R^{max}) are the minimal (maximal) radius (Å) from the nanoparticle center to the nanocluster relaxed outer shell (after geometry optimization with or without water monoshells). This roundness degree is essentially a positive value in the range [0;1] (dimensionless) : the closer

to 1 meaning an optimized nanoparticle outershell approaching the geometry of a sphere; the closer to 0 meaning an outershell approaching the geometry of an ellipsoid.

In order to quantify the influence of the adsorption of the water monoshells on the Au nanoparticle structures, we have calculated the variation of the roundness degree ΔS on the basis of the optimized nanocluster outershells with and without the presence of water. The corresponding variation is thus defined as follows :

$$\Delta S = S_{AuNP-NH2O} - S_{AuNP} \text{ [Eq. S6]}$$

where $S_{AuNP-NH2O}$ and S_{AuNP} are the roundness degrees with and without water monoshells, respectively. When ΔS is positive, the water monoshell has induced a significant geometric deformation of the nanocluster outershell from its symmetric structure in vacuum toward a globally rounder shape. At the opposite, when ΔS is negative, the resulting geometric deformation of the nanocluster outershell upon water adsorption is a stretching of the initial symmetric structure along the largest symmetry axis of the nanoparticle. When ΔS is close to zero, the nanocluster may have been slightly distorted upon water adsorption, however, in average, the deformation is negligible.

All the corresponding results have been exposed in Table S2 and Figure S17. As a first remark (see Figure S17), the influence of the adsorption of water monoshells on the nanocluster shape tends to decrease progressively with the size of the nanoparticle. From a general standpoint, the majority of the Au clusters have undergone a slight stretching of their structures (negative ΔS). Among the nine nanoclusters, only two of them have become rounder (Au_{38} (rto) and Au_{55} (ino), with positive ΔS) and two other ones have not been distorted significantly in average (Au_{54} (deca) and Au_{147} (ino), with ΔS being almost zero).

In the case of Au_{55} (ino) and Au_{147} (ino) with the presence of the water monoshells, the final and relaxed metallic geometries (icosahedral shape) are different from the clean initial structures (ino-

decahedral shapes). This morphology change is captured in the calculation of ΔS. For Au_{55} (ino), the change of morphology from ino-decahedral to icosahedral shape induced by the water monoshell explains the positive value of ΔS (the nanocluster being rounder). For Au_{147} (ino), this phenomenon is similar to a lesser extent.

Nanocluster	Au_{38} (rto)	Au_{54} (deca)	Au_{55} (ico)	Au_{55} (ino)	Au_{79} (ito)	Au_{105} (deca)	Au_{147} (ico)	Au_{147} (ino)	Au_{201} (rto)
$R^{min}_{AuNP-NH2O}$ (Å)	3.882	4.008	4.645	4.704	5.267	5.101	6.657	6.765	7.201
$R^{max}_{AuNP-NH2O}$ (Å)	5.784	6.896	5.727	5.570	6.464	9.339	8.421	8.816	8.982
$S_{AuNP-NH2O}$	0.671	0.581	0.811	0.845	0.815	0.546	0.790	0.767	0.802
R^{min}_{AuNP} (Å)	3.653	3.990	4.810	4.203	5.356	5.244	6.870	6.497	7.329
R^{max}_{AuNP} (Å)	5.769	6.900	5.441	5.678	6.424	9.213	8.291	8.570	8.855
S_{AuNP}	0.633	0.578	0.884	0.740	0.833	0.569	0.828	0.728	0.827
ΔS	0.038	0.003	-0.073	0.104	-0.019	-0.023	-0.038	0.009	-0.026

Table S2. Surface atom to center distance analysis: minimal $R^{min}_{AuNP-NH2O}$ and maximal $R^{max}_{AuNP-NH2O}$ radii (Å) from center to surface atom of solvated Au nanoparticles ("AuNP-NH2O"), minimal R^{min}_{AuNP} and maximal R^{max}_{AuNP} radii (Å) from center to surface atom of naked Au NP, roundness degree of solvated $S_{AuNP-NH2O}$ and naked Au NP S_{AuNP}, and the variation of roundness degree ΔS with and without water (dimensionless).

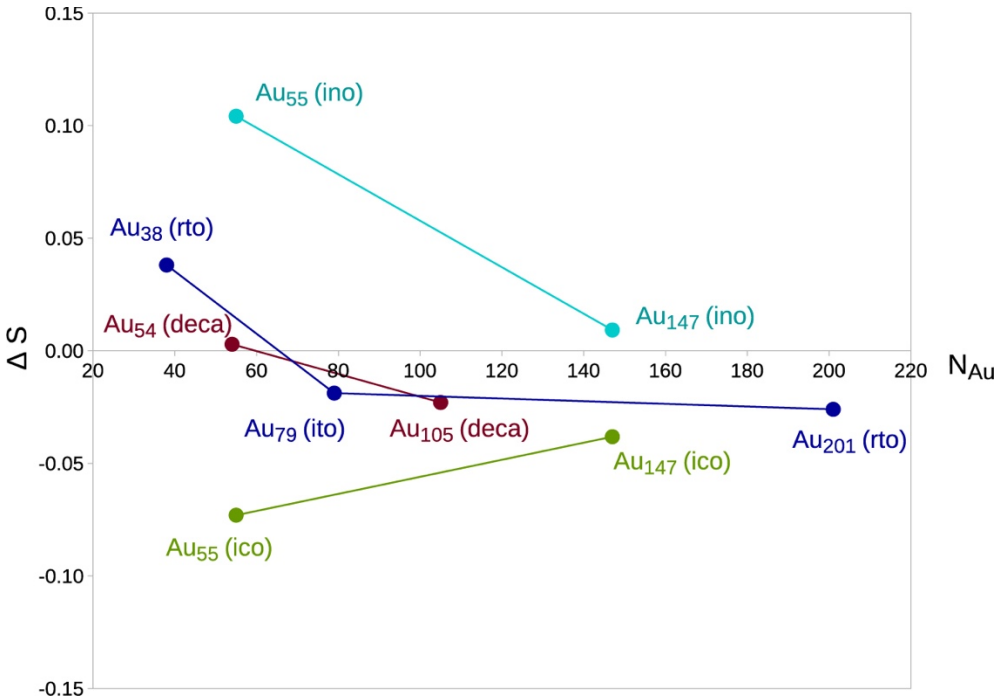

Figure S17. Evolution of the variation of the roundness degree ΔS (dimensionless) upon water adsorption (monoshells) as a function of the number of Au atoms (N_{Au}) present in the nine considered nanoparticles.

3.3/ Hydrogen Bonding Model

In this section, a theoretical model is developed to evaluate the part of the total hydrogen bond energy in the adsorption energy of water molecules surrounding the Au nanoclusters.

In our additive model, the total coadsorption energy ΔE_{coads}^{tot} for N_{H2O} water molecules present in the monoshell surrounding the Au NP is expressed following the additive model :

$$\Delta E_{coads}^{tot} = \Delta E_{deform}^{tot} + N_{chem}^{H2O} \Delta E_{int,chem}^{1H2O,best} + N_{phys}^{H2O} \Delta E_{int,phys}^{1H2O,best} + \Delta E_{int,H2O-H2O}^{tot} + N.A. \quad \text{[Eq.S7]}$$

where ΔE_{deform}^{tot} is the total deformation energy of Au NP and water molecules induced by the adsorption process, $\Delta E_{int,chem}^{1H2O,best}$ being the interaction energy of one water monomer chemisorbed on Au NP (best chemisorption structure), $\Delta E_{int,phys}^{1H2O,best}$ being the interaction energy of one water

monomer physisorbed on Au NP (best physisorption structure), $\Delta E_{int,H2O-H2O}^{tot}$ being the total interaction energy between water molecules in the monoshell, N_{chem}^{H2O} being the total number of chemisorbed water molecules, N_{phys}^{H2O} being the total number of physisorbed water molecules and N.A. being the non-additivity of the model.

The first approximation is the neglect of the non-additivity of the model. The second one is that the total interaction energy between the water molecules is identified as the total hydrogen bonding energy:

$$\Delta E_{int,H2O-H2O}^{tot} \approx \Delta E_{HB}^{tot} \text{ [Eq. S8]}$$

The last approximation is that the sum of total deformation energy and the interaction energy of chemisorbed and physisorbed molecules in the monoshell is expressed as N_{H2O} times the interaction energy of one chemisorbed water monomer (best chemisorption form) on the Au NP:

$$N_{H2O}\Delta E_{ads}^{1H2O,best} \approx \Delta E_{deform}^{tot} + N_{chem}^{H2O}\Delta E_{int,chem}^{1H2O,best} + N_{phys}^{H2O}\Delta E_{int,phys}^{1H2O,best} \text{ [Eq. S9]}$$

This means that chemisorbed and physisorbed molecules are initially not differentiated. As a consequence, the total coadsorption energy reads:

$$\Delta E_{coads}^{tot} = N_{H2O}\Delta E_{ads}^{1H2O,best} + \Delta E_{HB}^{tot} \text{ [Eq. 10]}$$

Hence in our model, the total hydrogen bonding energy between water molecules in the adsorbed monoshell is calculated according to the following formula and associated Figure S18:

$$\Delta E_{HB}^{tot} = E_{tot,OPT}^{NH2O,GEO2} - \left(N_{chem}^{H2O}E_{tot,OPT}^{1H2O,GEO1} + N_{phys}^{H2O}E_{tot,OPT}^{1H2O,GEO3} + (1 - N_{chem}^{H2O})E_{tot,SPE}^{1AuX,GEO1}\right) \text{[Eq. S11]}$$

where $E_{tot,OPT}^{NH2O,GEO2}$ is the total electronic energy of the complete relaxed system (water monoshell and Au_X) noted "OPT.GEO2", $E_{tot,OPT}^{1H2O,GEO1}$ being the total electronic energy of the best chemisorption form of one water monomer on Au_X, noted "OPT.GEO1", $E_{tot,OPT}^{1H2O,GEO3}$ being the total electronic energy of the optimized isolated water molecule in gas phase, noted "OPT.GEO3", and $E_{tot,SPE}^{1AuX,GEO1}$ being the total electronic energy of the deformed and isolated Au_X nanocluster

(without water) in the geometry "OPT.GEO1" (single point energy calculation noted "SPE.GEO1"). This means that physisorption is neglected in our approximated model.

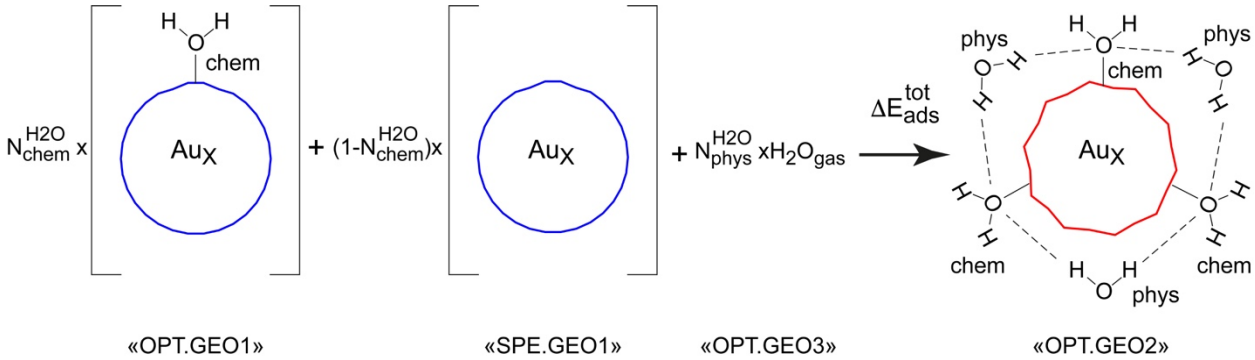

Figure S18. Hydrogen bonding model for the water monoshells decorating the various Au nanoclusters (X atoms, X being 38, 54, 55, 79, 105, 147, 201). OPT.GEO1 is the optimal geometry of the water monomer chemisorbed on the Au_X nanocluster (best chemisorption form). SPE.GEO1 is the same geometry of OPT.GEO1 used to calculate the energy of the isolated and deformed Au_X nanocluster (single point energy). OPT.GEO2 is the optimal geometry of the water monoshell surrounding the Au_X nanocluster. OPT.GEO3 is the optimized isolated water molecule in gas phase. N_{chem}^{H2O} and N_{phys}^{H2O} are the numbers of chemisorbed and physisorbed water molecules, respectively.

The hydrogen bond energy is then derived by normalizing the total hydrogen bonding energy by the number of water molecules:

$$E_{HB} = \frac{\Delta E_{HB}^{tot}}{N_{H2O}} \text{ [Eq. S12]}$$

The number of hydrogen bonds per water molecule in the monoshell is finally evaluated by dividing the normalized hydrogen energy E_{HB} by the water dimerization energy $E_{H2O\ dimer}^{gas}$ calculated for two water molecules in the gas phase (-0.256 eV at the PBE-D3 level):

$$N_{HB} = \frac{E_{HB}}{E^{gas}_{H2O\ dimer}} \text{ [Eq. S13]}$$

All these results are exposed in the Table S3.

Nanocluster	Au38 (rto)	Au54 (deca)	Au55 (ico)	Au55 (ino)	Au79 (ito)	Au105 (deca)	Au147 (ico)	Au147 (ino)	Au201 (rto)
N_{H2O}	65	96	77	79	110	148	160	158	212
N^{H2O}_{chem}	14	17	17	17	19	22	29	29	28
N^{H2O}_{phys}	51	79	60	62	91	126	131	129	184
$\Delta E^{1H2O,best}_{ads}$ (eV)	-0.385	-0.399	-0.416	-0.459	-0.338	-0.387	-0.310	-0.338	-0.346
ΔE^{tot}_{coads} (eV/H_2O)	-0.608	-0.639	-0.611	-0.607	-0.632	-0.623	-0.643	-0.627	-0.642
E_{HB} (eV/ H_2O)	-0.516	-0.566	-0.509	-0.489	-0.571	-0.564	-0.585	-0.572	-0.595
N_{HB}	2.181	2.388	2.151	2.063	2.412	2.381	2.469	2.417	2.512

Table S3. Hydrogen bonding model for water monoshells on Au NPs : total number of water molecules N_{H2O}, number of chemisorbed N^{H2O}_{chem} and physisorbed N^{H2O}_{phys} water molecules, adsorption energy of best chemisorption form for water monomer $\Delta E^{1H2O,best}_{ads}$, normalized coadsorption energy per water molecule in the monoshell ΔE^{tot}_{coads}, hydrogen bonding energy per water molecule E_{HB} and number of hydrogen bonds per water in the monoshell N_{HB}.