

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

**Multiple NO adsorption on Au_{10}^- and Au_9Zn^- planar clusters.
A comparative DFT study**

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1. Test of the RPBR functional, with the settings on our computer code SIESTA, for properties of $(\text{NO})_2$ dimer.
2. Lowest energy isomers of $\text{Au}_{10}(\text{NO})_n^-$ and $\text{Au}_9\text{Zn}(\text{NO})_n^-$ for $n=0-6$ compounds are given in Figures 1 and 2, respectively. The excess energy with respect to the total energy of the ground state is smaller than 0.15 eV in all cases, and is given together with the spin multiplicity ($M = 2S + 1$) in parenthesis.

Test of RPBE functional

A very critical test for high level quantum chemistry calculations is the prediction of the ground state structure, and the dissociation energy to two NO molecules, of the gas phase (NO)₂ dimer ¹. In the Supporting Information (SI) are compared the results of RPBE functional and our settings against experiments and high level calculations. The experimental ground state is a planar singlet of two NO in *cis* form, with N-N and N-O distances 2.24-2.33 Å and 1.15-1.16 Å, respectively, and NN-O angle of 95-100° ¹. The experimental binding energy of the two NO is difficult of measure because the intermolecular frequencies and 0 K binding energy. Ivanic and coworkers ¹ give 0.1214-0.1648 eV as a best estimation. High level quantum chemistry calculations, using multireference second order perturbation theory (MRMP2), achieve good agreement with that energy and distances, but predict the *trans* structure of (NO)₂ instead of the *cis* one. On the other hand, DFT methods predict binding energies far from experimental estimates. For example, a meta-GGA/PLAP1/6-311G+(d) calculation ² predicts a triplet *trans* state with binding energy 0.355 eV, and N-N and N-O distances 2.121 Å and 1.161 Å, respectively. Our GGA/RPBE calculation, predict the experimental singlet *cis* form as the ground state, but with binding energy 0.340 eV and N-N and N-O distances 2.023 Å and 1.185 Å, respectively.

REFERENCES

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- 2 H. A. Duarte, E. Proynov and D. R. Salahub, J. Chem. Phys., 1998, 109, 26.

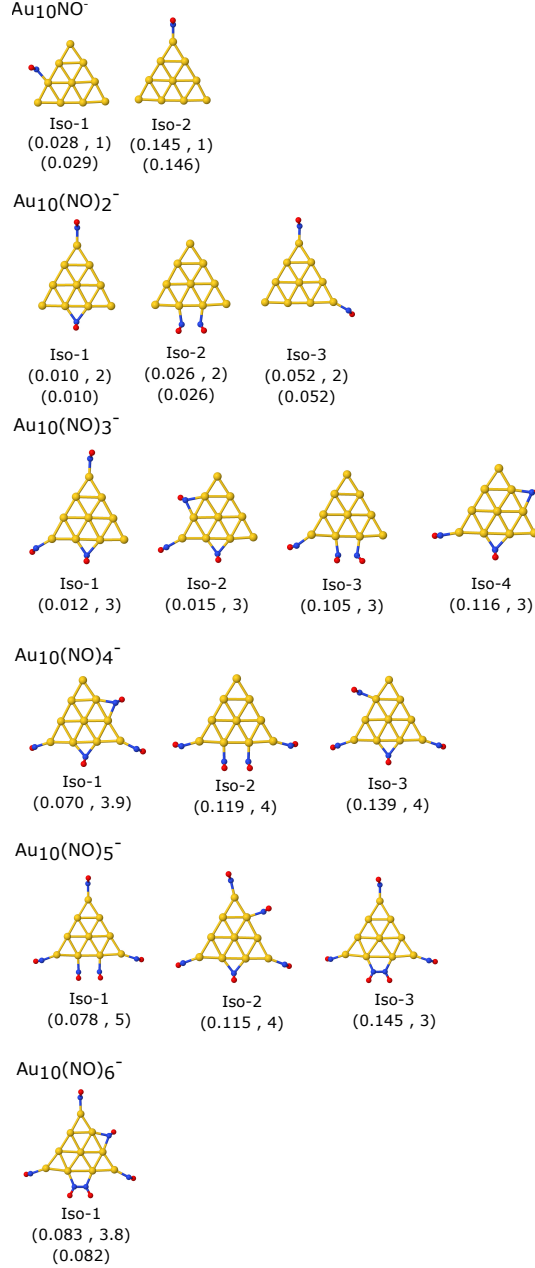


FIG. 1. Some representative low energy isomers of Au₁₀(NO)_n⁻ for n=1-6 compounds. The excess energy with respect to that of the ground state geometry, and the multiplicity M=2S+1, are given in brackets. Note, for instance, the variety of adsorption geometries and spin multiplicities of the isomers Iso-1, Iso-2, and Iso-3 of Au₁₀(NO)₅⁻ as compared with the features of the ground state given in the main paper. Note also the formation of a *cis* (NO)₂ dimer on bridge site of an edge in both the Iso-3 of Au₁₀(NO)₅⁻ and the Iso-1 of Au₁₀(NO)₆⁻, at 0.145 eV and 0.094 eV excess energy, respectively. Below of the isomers of Au₁₀(NO)⁻, Au₁₀(NO)₂⁻, and Au₁₀(NO)₆⁻ is given (in parenthesis) the excess energy when calculations are performed with an energy cutoff of 350 Ry and a force tolerance window of 0.0015 eV/Å, which indicates that our calculations are precise enough (within 0.001eV) and the structures in Figure 1 of the main text are robust.

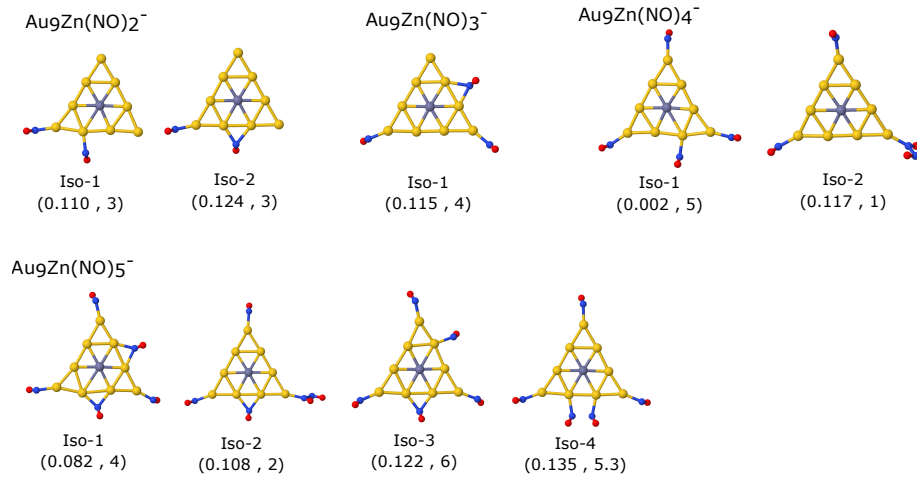


FIG. 2. Some representative low energy isomers of $\text{Au}_9\text{Zn}(\text{NO})_n^-$ for $n=2-5$ compounds. The excess energy with respect to the ground state energy and the multiplicity $M=2S+1$ are given in brackets. Notice, for instance, the formation of a *trans* $(\text{NO})_2$ dimer *on top* of a corner for the isomers Iso-2 of $\text{Au}_9\text{Zn}(\text{NO})_4^-$ and Iso-2 of $\text{Au}_9\text{Zn}(\text{NO})_5^-$, both at more than 0.1 eV excess energy.