Adsorption of the Nihonium Species on Gold Surface: a Relativistic Density Functional Theory Study

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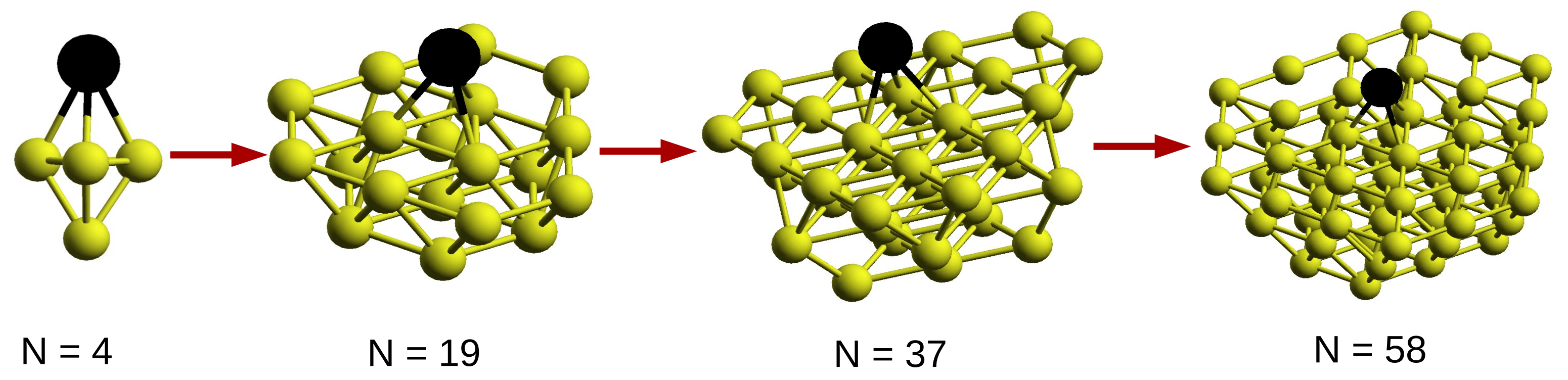
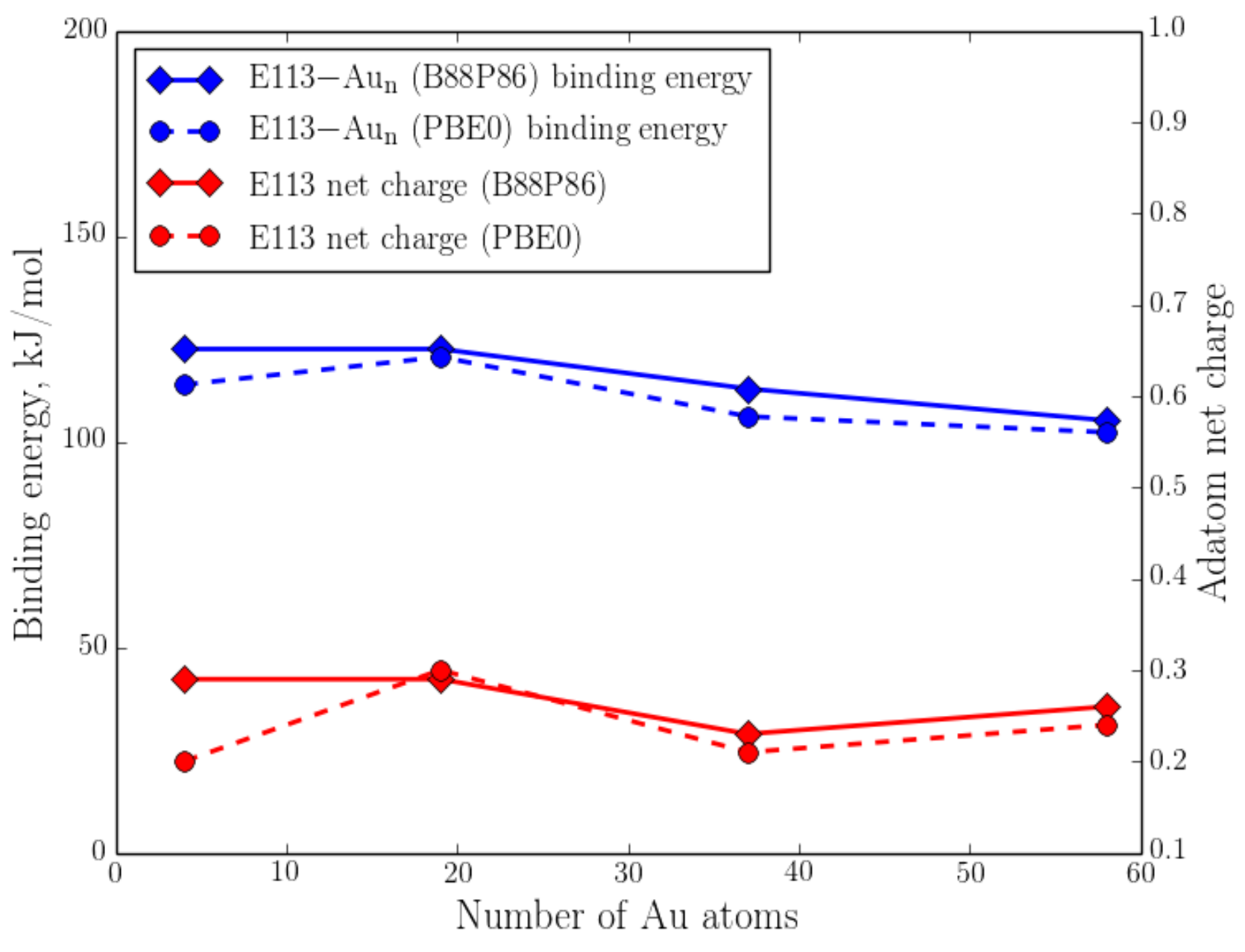
The discovery of long-lived isotopes of superheavy elements (SHEs) in nuclear fusion reactions of ^{48}Ca with actinide targets signifies a close approach to the island of particularly shell-stabilized nuclei. While the emergence of the new elements is a fantastic discovery itself, the longevity of certain isotopes is thought-provoking for chemical investigations, both experimental and theoretical. Successful chemical identification of copernicium (element 112, Cn) and flerovium (element 114, Fl) has been recently followed by the recognition of the discovery of nihonium (element 113, Nh) confirmed at the fourth IUPAC/IUPAP Joint Working Party. Although preliminary experimental results have been recently obtained in FLNR JINR (Dubna), the chemical properties of nihonium remain of top interest. From the theoretical standpoint, investigations of the SHE chemistry are especially challenging as they require an understanding of the electronic structure in the presence of strong fields of heavy nuclei and thus governed by relativistic effects.

Nihonium single atoms adsorption on gold surface



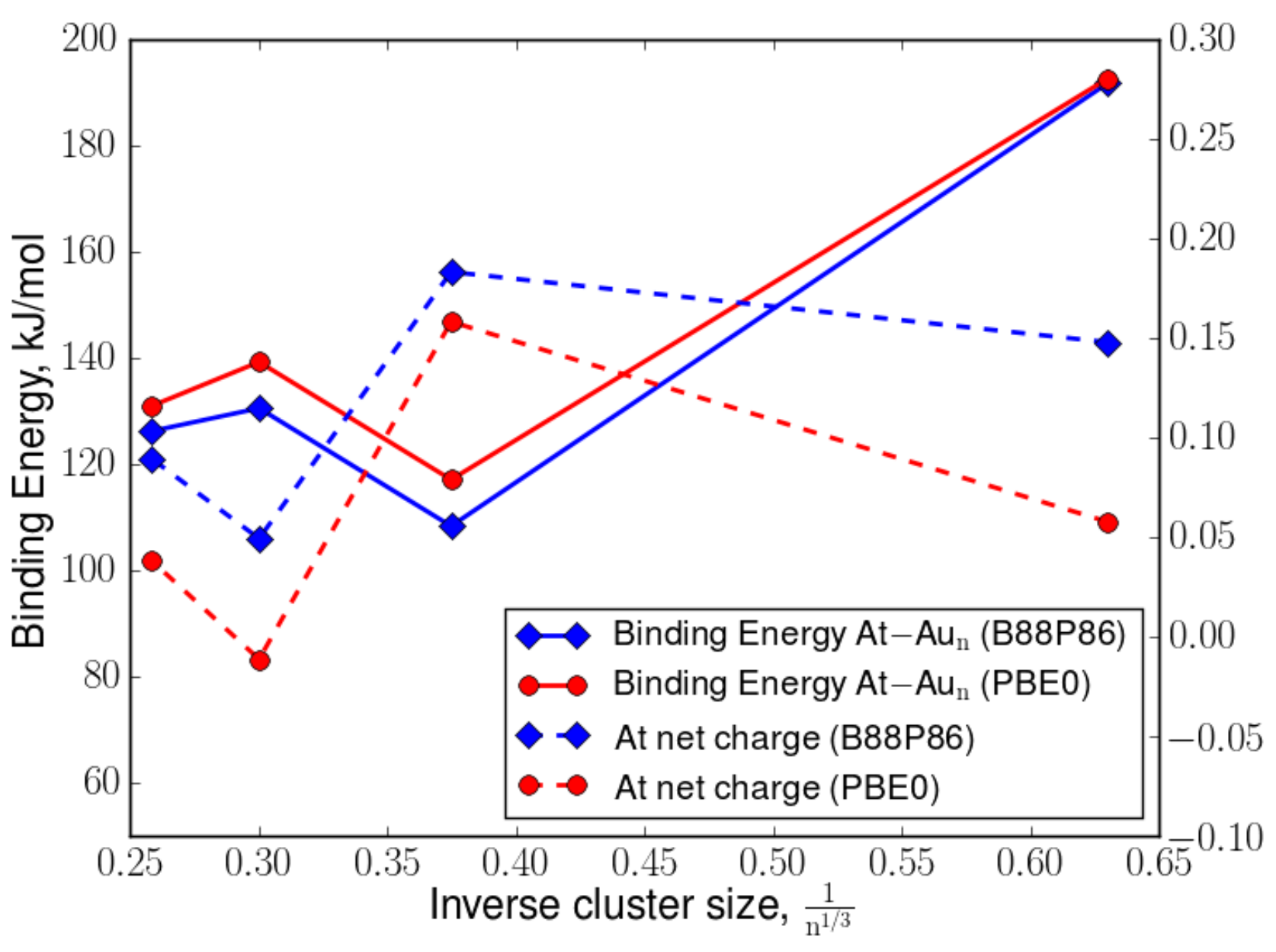


Several gold clusters comprising up to 58 atoms were chosen to simulate the adsorption site of Nh on the stable (111) gold surface. According to a series of preliminary calculations, the hollow-2 position of the adatom is energetically preferable. Since the stabilization of binding energies upon the increase of n can be occasional, the convergence was additionally monitored through analyzing Bader net charges of the adatom and neighboring Au atoms and equilibrium distance adatom/gold surface as functions of the cluster size. The figure illustrates the dependence of the calculated Nh–Au$_n$ binding energy and the Nh net charge on the cluster size. The resulting adsorption energy estimates lie within the range **106±10 kJ/mol**. Experimental estimation for adsorption energy of the Nh formal homologue Tl on gold surface is **270 ± 10 kJ/mol**.

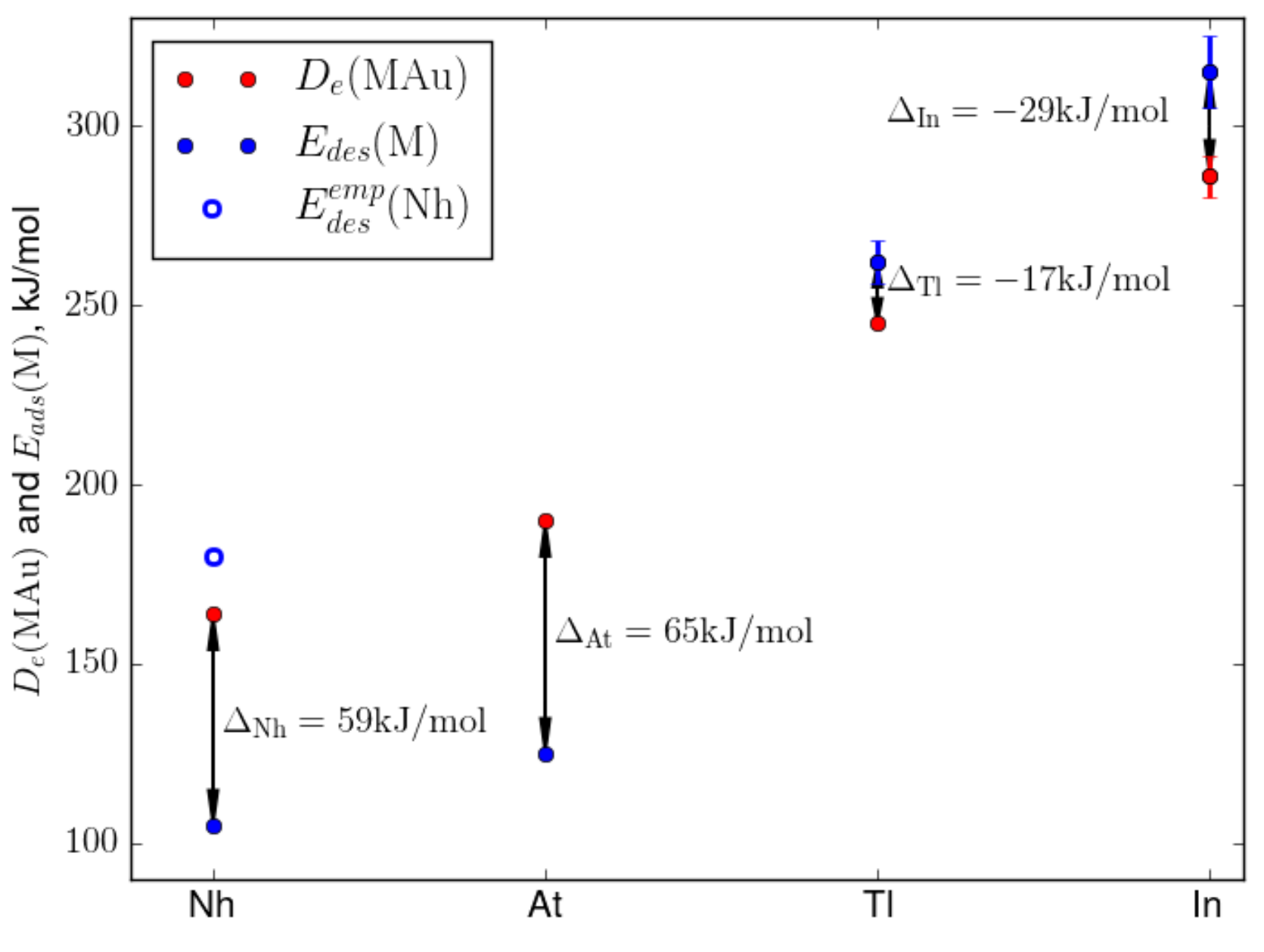
7th Period Subperiodic Structure

It has been shown experimentally that the adsorption temperatures and energies of Cn and Fl atoms on a gold surface are fairy close to each other and overall lower than those of their immediate homologs Hg and Pb, observed on the same surface. This confirms theoretical predictions concerning the electronic structure of Cn and Fl atoms: the strong relativistic stabilization of the s and $p_{1/2}$ shells in both Cn ($6d^{10}7s^2$) and Fl ($6d^{10}7s^27p^2{}_{1/2}$) results in a closed-shell character of the ground states of these atoms. Due to this unique feature of the 7th row of the Periodic Table, the electronic structure of a Nh atom can be interpreted as a Fl atom with a hole in its closed $7p_{1/2}$ subshell. This observation seems to render astatine a closer chemical “relative” of Nh in comparison to the formal homologue Tl. Thus, At might be a plausible chemical species for model experiments aiming at finding the optimum experimental conditions for further explorations of the Nh chemistry.

Astatine single atoms adsorption on gold surface



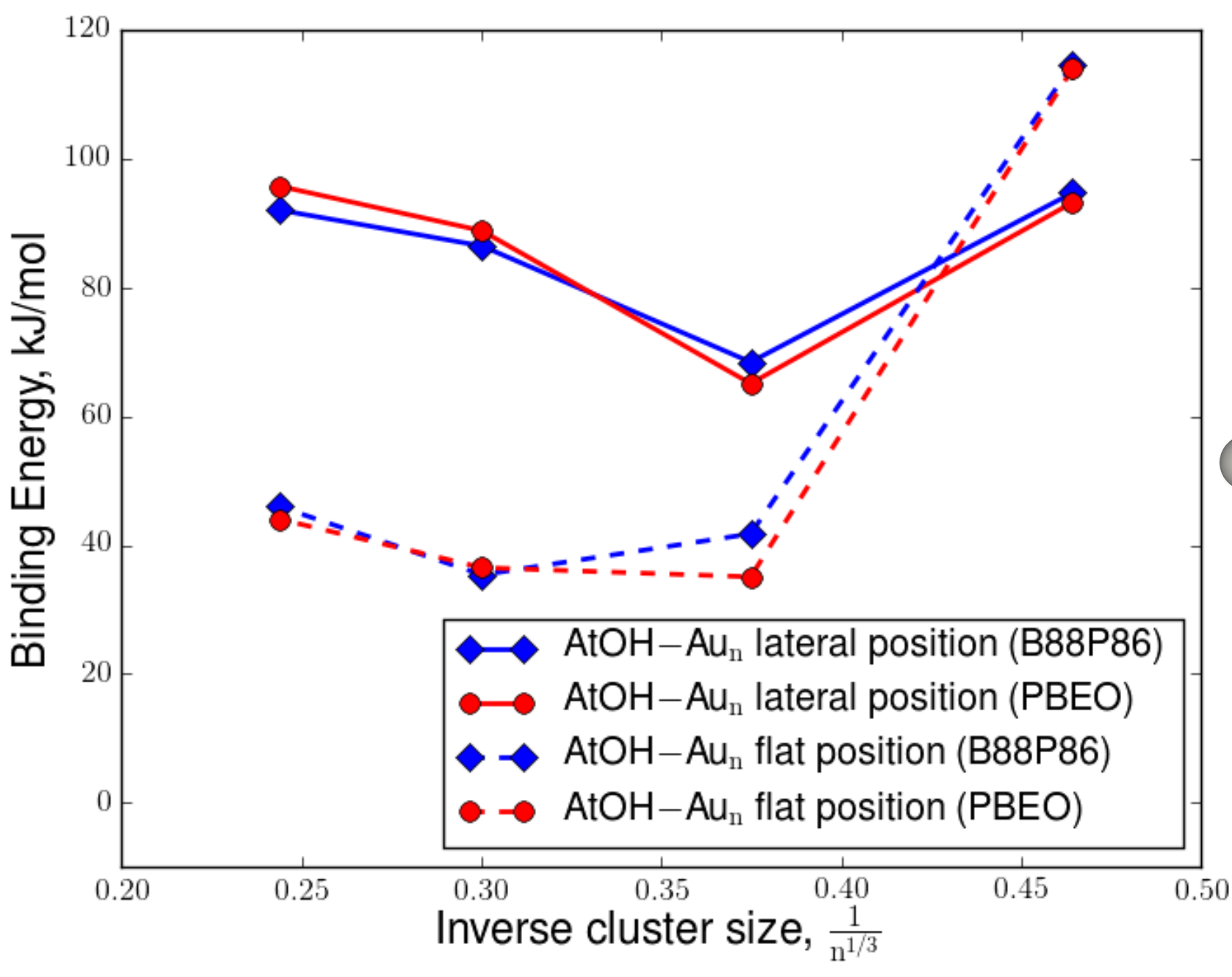
The adsorption energy of elemental astatine on a stable gold (111) surface is estimated using gold clusters with up to 69 atoms in order to simulate the adsorption site. To simulate the electronic structure of At−Au$_n$ complexes, we combine accurate shape-consistent relativistic pseudopotentials and non-collinear two-component relativistic density functional theory. The predicted adsorption energy for At on gold is **130 ± 10 kJ/mol**. This value agree with the data based on experimental findings **147 ± 15 kJ/mol**, thus confirming the correctness of the interpretation of the experimental data.

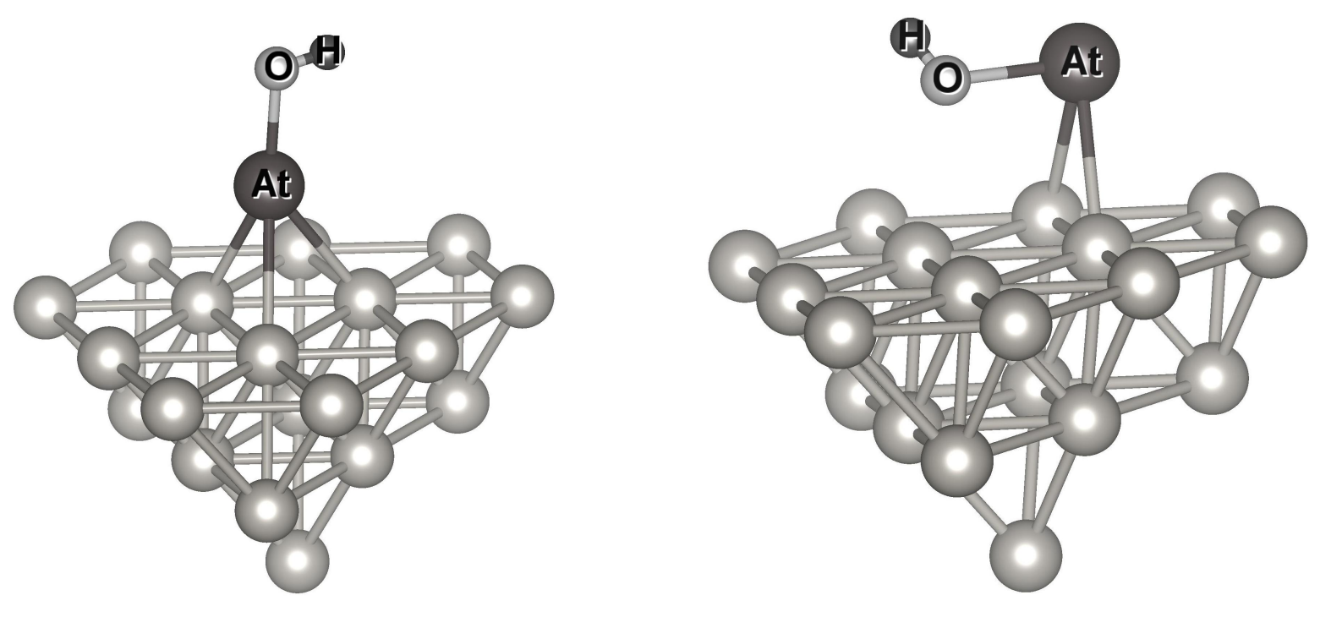


Comparison of the dissociation energies D_e(MAu) [kJ/mol] of MAu *molecules with the adsorption energies* E_{ads}(M) *[kJ/mol] of single* M *atoms on a gold surface, where* M = Nh, At, Tl, and In. *The corresponding differences in binding energies* Δ_M *[kJ/mol] are indicated for each considered element. Experimental data are presented with error bars, whereas the theoretical results were obtained within the 2c-RDFT (B88P86) approach.*

The differences between the dissociation energy of a MAu molecule (with M = Nh and At) and the respective adsorption energy of single atoms of M on the surface of a gold cluster are stable and amount to approximately 60 kJ/mol. For Tl and In, assumption of “constant differences” holds too, however with differences of another magnitude and an opposite trend (i.e., -20 kJ/mol). Based on these differences from the immediate homologs Tl and In, one obtains an adsorption energy for Nh atoms on gold of **E^{Au}_{ads} (Nh) ≈ 180 kJ/mol**. This result coincides with previous semi-empirical evaluations. However, the question arises, whether these results hold for adsorptions at high temperatures. **The adsorption behavior of adatoms on a hot surface can be rather different from the adsorption on a cold one.**

AtOH molecules adsorption on gold surface

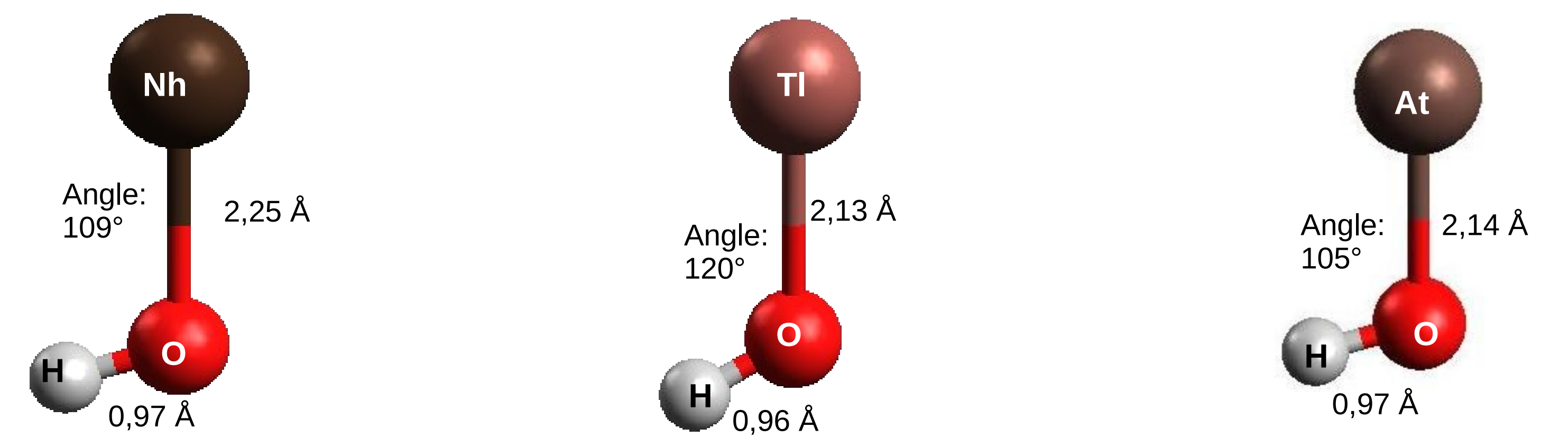




The binding energy of an AtOH molecule with gold clusters consisting of more than 19 atoms (i.e., less than 0.37 in terms of inverse cluster size) in the flat position lies within the 50 – 30 kJ/mol range. This is substantially lower, than that obtained for the lateral AtOH position with binding energies between **80 – 100 kJ/mol**. Generally, the charge transfer in AtOH−Aun adsorption complexes is stronger than the one occurring in At−Aun; the gold clusters act as an electron donor. This value also agree with the data based on experimental findings **100^{+20}_{-10} kJ/mol**.

Molecular structures and properties of NhOH, AtOH and TlOH

Electronic structure of NhOH, TlOH and AtOH molecules was studied within the accurate relativistic small-core pseudopotential model, using high-level scalar relativistic coupled cluster method for correlation treatment and non-collinear two-component density functional theory for incorporating the effects of spin-dependent relativistic interactions. The resulting estimate for the hydroxyl group elimination enthalpy from NhOH at 0 K is 188 kJ/mol, being quite close to that for AtOH and much smaller than the corresponding value for the monohydroxide of the formal homologue, Tl. Bader net charge distributions for NhOH and AtOH molecules are quite similar, $Nh^{+0.48}O^{-0.99}H^{+0.51}$ and $At^{+0.42}O^{-0.98}H^{+0.56}$. The charge transfer in TlOH more pronounced, $Tl^{+0.69}O^{-1.24}H^{+0.55}$. Presented data for NhOH and TlOH molecules agrees reasonably with previous 4c (fully relativistic) DFT results.



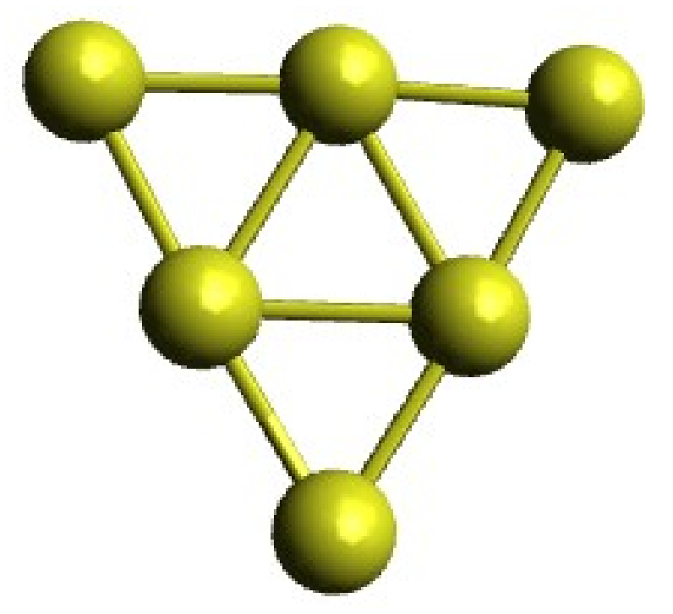
Nh — OH:
$-\Delta H_0$ = 188 kJ/mol

Tl — OH:
$-\Delta H_0$ = 319 kJ/mol

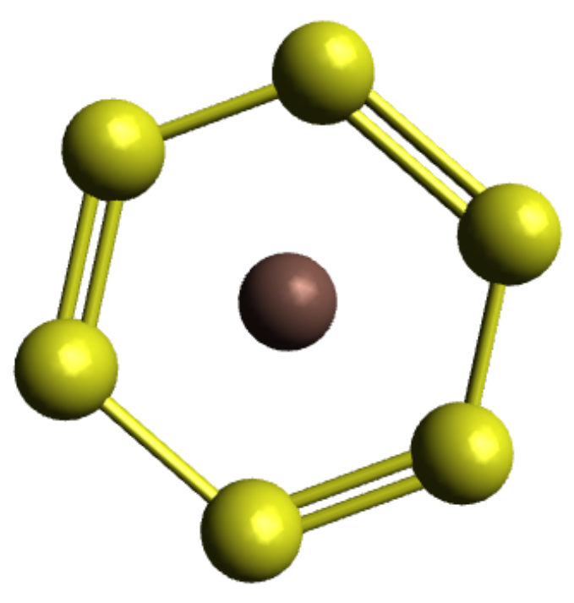
At — OH:
$-\Delta H_0$ = 174 kJ/mol

The performed calculations confirm the experimental observation on the formation of AtOH molecules in presence of trace amounts of water and oxygen in the carrier gas. Due to the previously discussed similarities in the chemical properties of AtOH and NhOH molecules, one may expect, that the formation of NhOH is indeed possible under experimental conditions similar to those in the experiments on At.

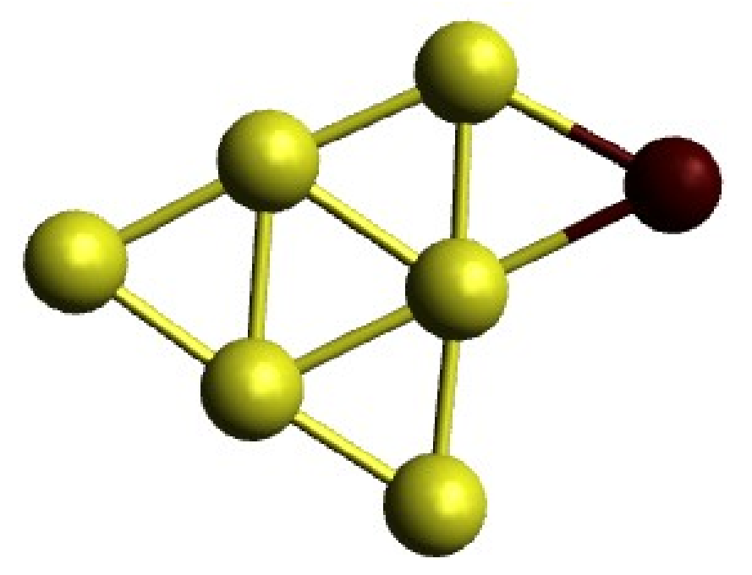
Nihonium electronegativity



Neutral Au_6 cluster



$At^+Au_6^-$ cluster



$NhAu_6$ cluster
without sufficient for Au_6 ring
formation charge transfer

It was already shown that Nh atom is negatively charged in diatomic NhTs molecule, where Ts is the heaviest halogen. Although, Nh atom is electron donor in NhAt molecule, but in complex with Au_6 cluster charge transfer from Nh is insufficient for Au_6 ring formation. We guess that the oxidation state of At atom in At@Au_6 complex is greater than +1, such oxidation state for Nh atom is energetically unpreferable.

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Literature

S.N. Dmitriev et al., Mendeleev Commun., **24**, 253 (2014);
A. Serov et al., *Radiochim. Acta,* **101***, 421* (2013);
A. Serov et al., *Radiochim. Acta,* **99**, 593 (2011)*;*
V. Pershina Inorg. Chem., **57**, 3948 (2018)*;*
V. Pershina, J. Anton, T. Jacob, Chem. Phys. Lett. **480**, 157 (2009)*;*
A.V. Titov, N.S. Mosyagin, IJQC **71**, 359 (1999);
N.S. Mosyagin et al., Progr. Theor. Chem. Phys. **B 15**, 229 (2006);
C. van Wüllen, Z. Phys. Chem. **224**, 413 (2010);
A.A. Rusakov et al., Int. J. Quantum Chem., **11**, 1537 (2013);
Yu. Demidov, A. Zaitsevskii *Chem. Phys. Lett.* ***638****, 21* (2015);
Yu. Demidov, A. Zaitsevskii *Chem. Phys. Lett.* **691**, 126 (2018);

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