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DFT STUDY OF P-BLOC ELEMENTS ADSORPTION ON PAHs SURFACE: IMPLICATIONS FOR CLUSTER DESORPTION AND TEMPLATE-DIRECTED ASSEMBLY

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Abstract (& Background)

Density Functional Theory (DFT) calculations have been carried out to investigate the adsorption of metal and metalloids onto the polycyclic aromatic hydrocarbons (PAHs) surface and desorption of formed clusters from the surface of PAHs. DFT study of desorption of p-block metals and metalloids from PAHs is important for develop new applications in nanotechnology, environmental science, and materials engineering [1]. Desorption governs how reliably you can place, fix, and then release metal/metalloid nano-objects templated by PAHs which is a key for bottom-up metamaterial fabrication. Weak, tunable PAH–metal adhesion allows the formation of the size-/shape-selected clusters on aromatic templates, then desorb/transfer them to target substrates or matrices.

We performed a systematic density functional theory investigation (DFT: PW91/DNP; Charge = 0, singlet; Unrestricted Spin Polarization; Cutoff_Global = 4.8 Å; Opt_energy_convergence = 10-5) on the adsorption of Ga atoms on Phe using the GGA exchange-correlation functional PW91 [2], and considering the van der Waals interactions by Tkatchenko-Scheffler scheme [3].

Aims

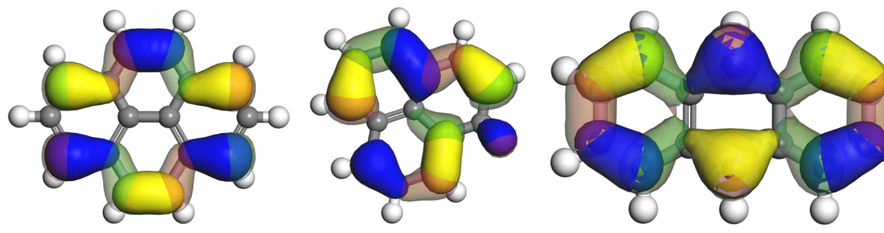
- ❑ Map preferred adsorption sites and orientations on representative PAHs (anthracene, phenanthrene, phenalene, pyrene).
- ❑ Benchmark metals (Al, Ga, In, Tl) and selected metalloids (e.g., Si, Ge, As, Sb) to build periodic trends in adsorption, charge transfer, and mobility;
- ❑ Evaluate how PAH size/shape shift HOMO/LUMO and modulate interaction strength;
- ❑ Quantify adsorption energies for single atoms and small clusters and extract size-dependent binding trends;
- ❑ Determine equilibrium geometries, contact areas, and contact angles of clusters on PAHs.

Method

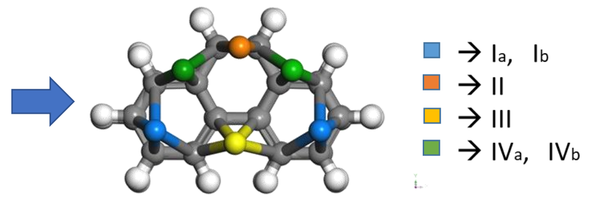
In this work, only a few of the studied structures were used for exemplification. For this investigation, the energies of over 4000 structures were studied and calculated. The notation M(n,m)-PAH (M = metal, PAH = polyaromatic hydrocarbon) was used, where n and m represent the number of M atoms placed to interact on each face of PAH. The Ga atoms were successively attached to the PAH surface until the M-M interactions led to the formation of clusters on the PAH surface. Each time, after the addition of each M atom, the M-PAH structure was reoptimized. Each time the M atom was added taking into account the previously used coordinates.

Results

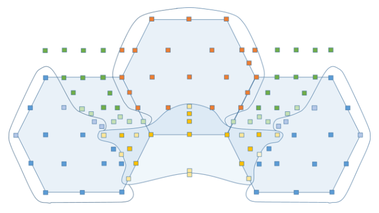
Pyrene (Pyr) **Phenalene (Pnl)** **Anthracene (Ant)** **Phenanthrene (Phe)**

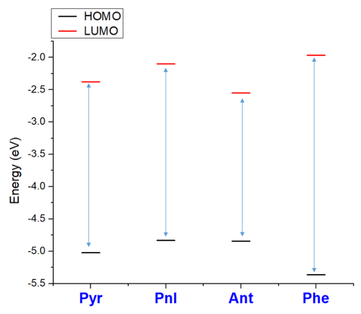


Map preferred adsorption sites and orientations on Phe



Hexagonal Grid for Ga(1,0)-Phe obtained by simulations by adding Ga atom in different positions on Phe surface





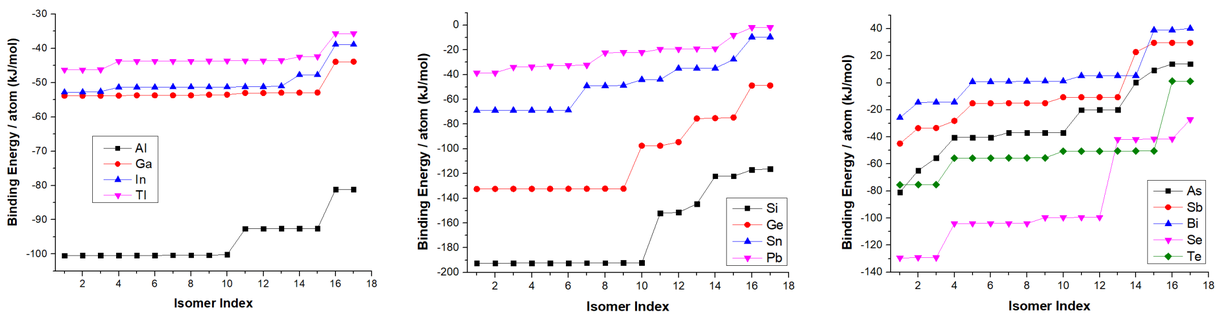
The plot of the frontier orbitals HOMO and LUMO (for an isovalue of 0.03) for the studied chem-ical structures. The surfaces are drawn by yellow/blue and green/red colors for HOMO and LU-MO, respectively, where the negative/positive blobs are represented by light and dark colors. The grey and white spheres represent the carbon and the hydrogen atoms.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular or-bital (LUMO), indicates the shapes and distributions of these orbitals, showing where the electron density is concentrated in the considered PAHs.

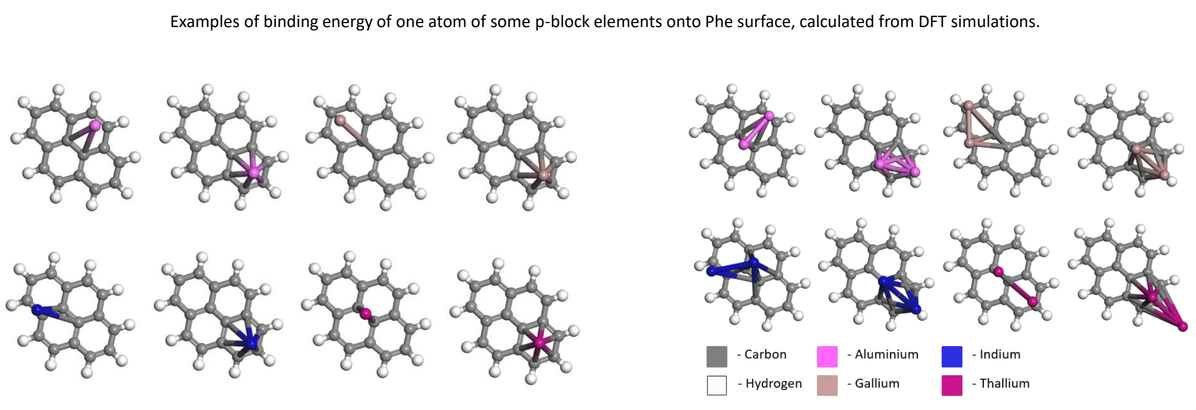
Pattern of interaction

HOMO: contributes mainly to Pauli repulsion ("pushback"/"pillow" effect). Electron density in occupied π orbitals repels metal spill-out electrons, causing a depletion just above the metal surface and a corresponding accumulation closer to the metal, which typically lowers the metal work function by ~0.2–0.8 eV.

LUMO: acts as a polarization/acceptor channel. There can be a very small induced occupancy (fractional, not integer) of π* character at the interface, visible in theory as faint PDOS weight above EF and in charge-density-difference plots as a slight accumulation over the ring.

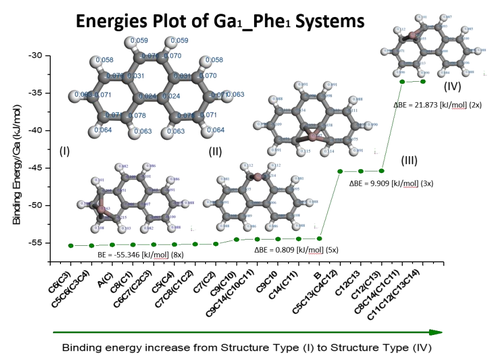


Examples of binding energy of one atom of some p-block elements onto Phe surface, calculated from DFT simulations.

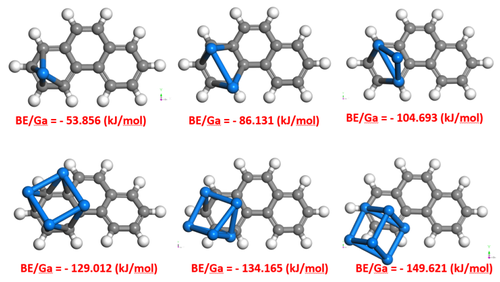


The left panel represents the absorption of a metal atom on the Pyr surface. The right panel represents the situation in which an identical metal atom is introduced into the system. It is observed that a certain position favors cluster formation for the Al, Ga and In atoms. The Tl atom does not meet the conditions to form a cluster on the Pyr surface.

Energies Plot of Ga_1_Phe_1 Systems

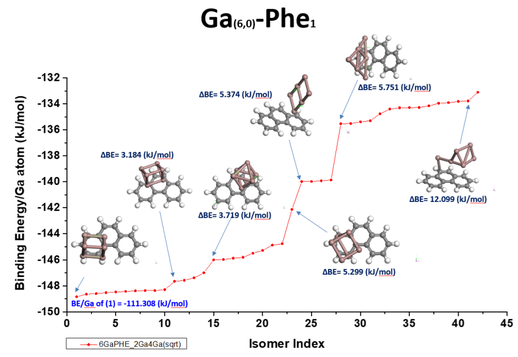


The Most Stable Ga-Phe Isomers

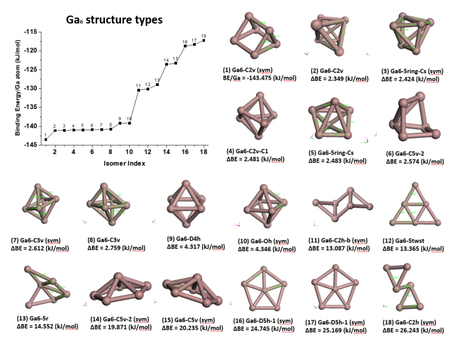


The most stable structures of the adsorption of Ga atoms on Phe molecule surface (blue - gallium atom, grey - carbon atom, white - hydrogen atom). In formula Ga(n,0) - Phe the first index represents the number of Ga atom on one face of Phe and the second index is the number of atoms on the second face.

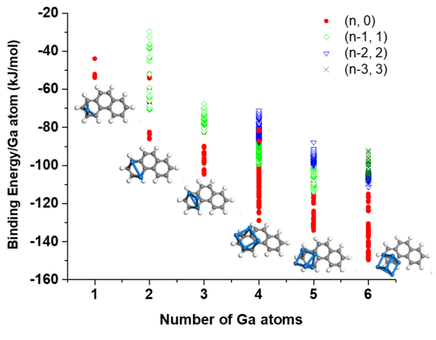
$Ga_{(6,0)}$-Phe_1

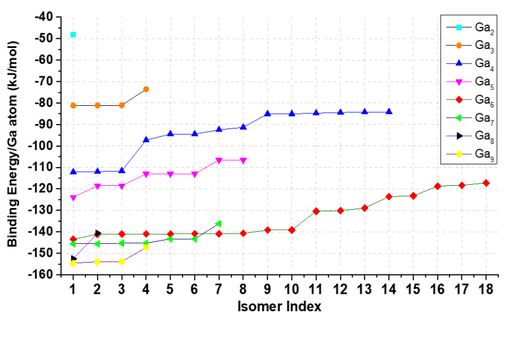


Examples of Ga – Phe structures containing the Ga atoms on one face of Phe rings. Ga(6,1)-Phe_1 represents a structure of six Ga atoms on Phe surfaces. In the plot, the dots connected by a solid line represent the calculated energy for a considered structure. The number in parentheses under the example structures represents the index number of the structure according to the energy increase. The values inserted in the figure present the values in kJ/mol for the energy variation of each structure compared to the most stable of the structures, for each of the Ga(n,m)-Phe types.



Binding energy per Ga atom of desorbed clusters of 6 Ga atoms from the surface of Phe.





Conclusions

- ❑ For small PAHs physisorbed on Al, Ga, In, Tl: neither HOMO nor LUMO "dominates" real charge transfer. Both only participate virtually (through polarization), so the interaction is mainly dispersion plus Pauli pushback with tiny fractional charge rearrangement;
- ❑ Weak physisorption with minimal hybridization; electrons contribute via pushback and polarization, not true transfer.
- ❑ Predominantly dispersion (van der Waals) plus Pauli "pushback"; only small, fractional charge transfer; Weak π–metal hybridization; interface dipole mainly from pushback;
- ❑ Preferred sites: Above ring centers (hollow) or bridge sites; registry tuned by PAH shape (bay vs armchair regions).
- ❑ Larger/heavier p-block atoms (In, Tl; Sn, Pb; Sb, Te) are more polarizable → somewhat stronger van der Waals attraction, but they also sit farther from the surface, which can partly offset gains. Al can bind comparably or a bit stronger than Ga–Tl because it has some partial covalent/ionic character;
- ❑ Rough qualitative order on considered PAHs: Al ≥ Ga ≈ In ≥ Tl; Si ≈ Ge ≳ Sn; Sb ≈ Te (differences are small);
- ❑ Larger PAHs give larger contact area and stronger adsorption energy; also slightly lower LUMO, enhancing polarization;
- ❑ Cluster adhesion scales with number of contact atoms and PAH size. Larger PAHs stabilize larger, flatter contact patches; small PAHs limit the footprint, promoting more spherical caps.

Discussion for Ga-Phe systems

- ❑ For all Ga1-6-Phe systems the stability increases with the increase of the number of Ga atoms on the one face of Phe;
- ❑ The energy of the systems increases in the order (n, 0)> (n-1, 1)> (n-2, 2)> (n-3, 3);
- ❑ The stable Ga-Phe systems contain flatter Phe;
- ❑ The Ga cluster of the most stable Ga-Phe are positioned on areas characterized by an electron delocalization (outer rings of Phe).
- ❑ Ga-Phe stability decreases with the linearity or flatness (less interactions between Ga atoms) of the Ga cluster on the Ga-Phe surface;
- ❑ There is an energetic balance between the deformation of Phe and the number of Ga atoms and how they are grouped on the surface Phe; the smaller deformation energy correspond to the Ga6-Phe systems.

Aknowledgements

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References

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[2] J. P. Perdew [et al.] Phys Rev B 46 (1992) 6671.
[3] A. Tkatchenko, M. Scheffler, Phys Rev Lett, 102 (2009) 073005.