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# Planar pentacoordinate germanium stabilized by the 18-valence-electron rule: structural and bonding comparison with silicon analogues

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This study examines the  $\text{SiE}_2\text{M}_3^{2+}$  and  $\text{GeE}_2\text{M}_3^{2+}$  clusters (E = P, As, Sb; M = Ca, Sr, Ba) stabilized by 18-valence-electron (18ve). Twelve global minima exhibiting  $C_{2v}$  symmetry were identified: six featuring a central silicon atom and six with a central germanium atom. All structures satisfy the geometric criteria for planar pentacoordination as defined by the IUPAC coordination concept. BOMD simulations at 298 and 600 K confirmed their kinetic stability. Using the central atom (Si or Ge) and the  $\text{E}_2\text{M}_3^{2+}$  ring as fragments, the EDA–NOCV analysis reveals that the orbital interaction term ( $\Delta E_{\text{orb}}$ ) constitutes the major contribution to stabilization. This is characterized by a dominant  $s(\text{Si/Ge})-\pi(\text{ring})$  coupling, accompanied by  $\pi$  reorganization, with no evidence of an independent Si/Ge–M  $\sigma$  bond. However, IQA analysis reveals that in  $\text{SiP}_2\text{M}_3^{2+}$ , all three Si–M interactions are repulsive, resulting in a planar dicoordinate silicon center. In  $\text{SiAs}_2\text{M}_3^{2+}$  and  $\text{GeP}_2\text{M}_3^{2+}$ , electrostatic repulsion involving one metal atom (M) prevents the formation of true pentacoordination, resulting instead in planar tetracoordinate centers. Only  $\text{GeAs}_2\text{M}_3^{2+}$  exhibits a genuine planar pentacoordinate germanium center, constituting the first confirmed example of this species stabilized by this specific electron count.

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## 1. Introduction

Systems with planar hypercoordinate atoms are rare and challenge the established principles of chemistry. Research in this field began with planar tetracoordinate carbon atom (ptC), which were initially proposed as a transition state in the interconversion of chiral molecules,<sup>1</sup> and later leading to strategies for its stabilization.<sup>2</sup> In 1991, Schleyer and Boldyrev introduced the first pentaatomic systems featuring a ptC, suggesting that stabilization requires a suitable cavity and strong bond with peripheral atoms.<sup>3</sup> Molecular orbital analysis later revealed that ptC stability arises from three C–ligand  $\sigma$  bonds, a delocalized  $\pi$ -system involving all five atoms, and additional ligand–ligand interactions, consistent with the 18-valence-electron (18ve) rule.<sup>4</sup> Although not a universal rule, given that several ptC structures with different electron counts

have been identified,<sup>5–8</sup> the 18ve principle remains an effective theoretical design strategy.<sup>4,9–12</sup> This principle has guided the design of numerous planar tetracoordinate carbon species, including those successfully synthesized or detected in the gas phase,<sup>13–18</sup> extending to other main group elements.<sup>12,19–21</sup>

For silicon and germanium atoms, which are isoelectronic analogs of carbon, both theoretical and experimental studies have demonstrated the feasibility of planar tetracoordination. The first experimental evidence was obtained from gas-phase photoelectron spectroscopy of  $\text{MAL}_4^-$  (M = Si, Ge), reported by Wang *et al.*<sup>22</sup> Subsequently, several ptSi and ptGe species have been synthesized in rigid or macrocyclic ligands.<sup>23–25</sup> From a theoretical standpoint, numerous studies have reported structures featuring a ptSi or ptGe center identified either as global or local minima, stabilized under different criteria. These include systems with halogenated transition-metal ligands  $\text{XM}_4\text{Cl}_4$  (X = Si, Ge; M = Ni, Pd, Pt),<sup>26</sup> structures with 18ve as  $\text{SiIn}_4^{2-}$ ,<sup>27</sup> pentaatomic structures with 14ve in  $\text{Li}_3\text{SiAs}^{2-}$ ,  $\text{HSiY}_3$  (Y = Al, Ga),  $\text{Ca}_3\text{SiAl}^-$ ,  $\text{Mg}_4\text{Si}^{2-}$ ,  $\text{C}_2\text{LiSi}$  and  $\text{Si}_3\text{Y}_2$  (Y = Li, Na, K);<sup>28</sup> planar triangular arrangements with  $D_{3h}$  symmetry in  $\text{X}_3\text{Cu}_3^+$ ,  $\text{X}_3\text{Li}_3^+$  (X = Si, Ge) and  $\text{X}_3\text{M}_3$  (X = C–Pb; M = Li–Cs) formed by three ptX units;<sup>29,30</sup> fan-like structures with  $C_{2v}$  symmetry in  $\text{C}_2\text{Si}_2\text{X}^q$ ,  $\text{XB}_2\text{Be}_2$  and  $\text{XB}_2\text{Bi}_2$  (X = C, Si, Ge, Sn, Pb;  $q = +1, 0, -1$ );<sup>31–33</sup> and, most recently, a ptSi in a rhombic arrangement in  $\text{Si}_3\text{Cu}_3^-$  with 16ve.<sup>34</sup> Despite progress in ptSi and ptGe, planar pentacoordinate silicon (ppSi) and

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germanium (ppGe) remain far less explored. Achieving planar pentacoordination is more challenging because the interactions between the central Si or Ge and neighboring metals are often weak or even repulsive, making it difficult to stabilize the system.

In 2020, the first ppSi and ppGe species were identified within the  $\text{XMg}_4\text{Y}^-$  ( $\text{X} = \text{Si}, \text{Ge}; \text{Y} = \text{In}, \text{Tl}$ ) and  $\text{SiMg}_3\text{In}_2$  systems.<sup>35</sup> These designs were based on the “electronic localization” approach, which consists of replacing one or two peripheral atoms in  $\text{XMg}_5^{2-}$  with more electronegative elements, to reduce electronic repulsion and strengthen X–Y bonding, thereby stabilizing the planar pentacoordinate center. In addition, several planar hypercoordinate configurations of silicon based on  $\text{SiO}_3$  units surrounded by alkali metals in  $\text{SiO}_3\text{M}^-$ ,  $\text{SiO}_3\text{M}_2$  and  $\text{SiO}_3\text{M}_3^+$  ( $\text{M} = \text{Li}, \text{Na}$ ) have been described, where EDA–NOCV bonding analysis reveals that the high stability and planarity in these systems is due to dative interactions ( $\text{M} \leftarrow \text{SiO}_3$ ) mediated by the metal s, p and d vacant orbitals, and Si–O multiple bonds.<sup>36</sup>

Building on this context, the 18ve rule is used here as a design guideline for achieving planar pentacoordination. This rule has been widely applied to predict numerous planar pentacoordinate carbon (ppC) species.<sup>37–44</sup> For instance, the  $\text{CO}_2\text{Li}_3^+$  cation has been reported to exhibit a global minimum with a ppC, when evaluated under the IUPAC coordination-number concept, along with interatomic distances and Wiberg bond indices.<sup>45</sup> However, a subsequent IQA analysis showed electrostatic repulsion between C and Li, indicating a planar dicoordinate carbon.<sup>46</sup> The same study extended the scope to  $\text{CE}_2\text{M}_3^+$  systems ( $\text{E} = \text{S–Te}; \text{M} = \text{Li–Cs}$ ), identifying five global minima with a ppC, all consistent with 18ve. Following this principle, we extend the design by replacing carbon with Si and Ge, substituting chalcogens with pnictogens ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ), and employing alkaline-earth metals ( $\text{M} = \text{Be–Ba}$ , Fig. 1). Systems containing Be or Mg exhibited imaginary vibrational modes and therefore did not correspond to real minima, while Ca, Sr, and Ba presented stable minima (see Tables S1 and S2). Unlike previous designs based on Mg and alkali metals, the heavier alkaline earth metals (Ca, Sr, Ba) offer a more favorable platform for 18ve-guided design with silicon or germanium centers. While all global minima satisfy the geometric criterion (IUPAC), only  $\text{GeAs}_2\text{M}_3^{2+}$  fulfills the energetic IQA criterion for genuine pentacoordination.

## 2. Computational details

This study focuses on a total of 30 pentaatomic combinations: fifteen with the formula  $\text{SiE}_2\text{M}_3^{2+}$  and fifteen with  $\text{GeE}_2\text{M}_3^{2+}$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}; \text{M} = \text{Be–Ba}$ ). All systems were designed to satisfy the 18ve rule. The initial structures were built with  $C_{2v}$  symmetry, placing the Si or Ge atom at the center. Geometry optimizations at the PBE0<sup>47</sup>-D3<sup>48</sup>/def2-TZVP level<sup>49</sup> revealed eighteen planar minima; the remaining combinations were discarded because harmonic frequency analysis revealed one or more imaginary vibrational modes (see Tables S1 and S2). These eighteen minima served as starting points for a more extensive potential energy surface (PES) exploration using a modified genetic algorithm implemented in the GLOMOS<sup>50,51</sup> program at the PBE0/SDDAll<sup>52,53</sup> level of theory. The search used an initial population of 80 candidate structures, applied 30 cross-over operations and 30 mutation operations in each generation, and proceeded for up to 10 generations. Isomers within 30 kcal mol<sup>−1</sup> were reoptimized at the PBE0-D3 level using aug-cc-pVTZ and aug-cc-pVTZ-PP (for Sb, Sr, and Ba),<sup>54–56</sup> harmonic frequency analysis confirmed them as true minima. Single-point energies were refined at the CCSD(T)<sup>57</sup>/aug-cc-pVTZ level, including zero-point energy corrections computed at the PBE0-D3/aug-cc-pVTZ level. Wavefunction stability checks and  $T_1$  diagnostics indicated negligible multireference character.<sup>58</sup> Finally, all singlet minima were recalculated as triplets to assess spin-state preferences.

The dynamical behavior of the system was explored through Born–Oppenheimer molecular dynamics (BOMD)<sup>59</sup> simulations at 298 K and 600 K, carried out at the PBE0-D3/SDDAll level for 20 ps with a 1 fs time step. Since this program implements only a velocity-rescaling thermostat *via* the ADMP method,<sup>60</sup> the simulations were run using the FULLSCF option to ensure equivalence with standard BOMD. All calculations were performed using the Gaussian 16.<sup>61</sup>

The electron distribution was evaluated using Wiberg bond indices (WBI)<sup>62</sup> and natural population analysis (NPA),<sup>63</sup> both implemented in NBO 7.0.<sup>64</sup> For a more detailed analysis of the nature of the bonds, the adaptive natural density partitioning (AdNDP)<sup>65</sup> method, implemented in Multiwfn, was used.<sup>66</sup> These calculations were performed at the PBE0-D3/aug-cc-pVTZ level, and the graphical representations were generated using VMD 1.9.3.<sup>67,68</sup>

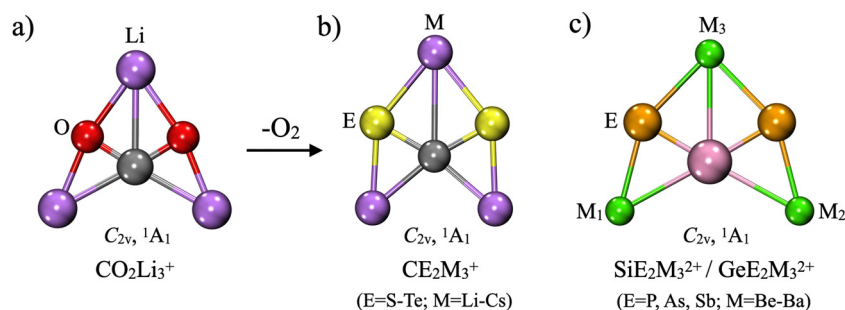


Fig. 1 Graphical representation of the global minimum ppC in (a) the  $\text{CO}_2\text{Li}_3^+$  cation and in (b) the  $\text{CE}_2\text{M}_3^+$  ( $\text{E} = \text{S–Te}; \text{M} = \text{Li–Cs}$ ) type systems. (c) The new  $\text{SiE}_2\text{M}_3^{2+}$  and  $\text{GeE}_2\text{M}_3^{2+}$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}; \text{M} = \text{Be–Ba}$ ) system proposed in this work.

Interatomic interaction energies ( $V_{\text{int}}$ ) were decomposed using the interaction quantum atoms (IQA) method.<sup>69</sup> This approach partitions  $V_{\text{int}}$  between atomic basins into a Coulomb term  $V_{\text{C}}$  (encompassing all classical electrostatic components) and an exchange–correlation term  $V_{\text{XC}}$  (capturing purely quantum contributions, including Pauli repulsion and electron correlation), which are commonly associated with ionic and covalent bonding, respectively. By convention,  $V_{\text{int}} < 0$  denotes attraction and  $V_{\text{int}} > 0$  denotes repulsion. All IQA calculations were performed in AIMAll<sup>70</sup> using wavefunctions generated at the PBE0-D3/aug-cc-pVTZ level.

Energy decomposition analysis (EDA) combined with ETS–NOCV was performed within the framework of relativistic density functional theory using the Amsterdam Density Functional (ADF 2024-103) code.<sup>71</sup> The zeroth-order regular approximation (ZORA)<sup>72</sup> was applied to account for scalar relativistic effects. Calculations were carried out using the PBE0-D3/TZVP<sup>73</sup> level. All systems were fragmented following the same scheme: one fragment corresponds to the central atom, and the second fragment corresponds to the surrounding “ring”. The interaction energy was decomposed according to the Morokuma–Ziegler scheme into the following components:

$$\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{elstat}} + \Delta E_{\text{disp}}$$

where int, Pauli, orb, elstat, and disp denote the total interaction energy, Pauli repulsion, orbital interaction (orbital mixing), electrostatic interaction, and dispersion correction, respectively.<sup>74,75</sup> Extended transition state (ETS) analysis was

combined with EDA to examine the decomposition of  $\Delta E_{\text{orb}}$ , and the characteristics of the orbital mixing terms. Each fragment is associated with a set of natural orbitals for chemical valence (NOCV),<sup>76</sup> and its deformation density,  $\Delta\rho$ , is represented by a sum of complimentary eigenfunctions ( $\Psi_{-k}, \Psi_{+k}$ ) weighted by their corresponding eigenvalues:

$$\Delta\rho = \sum \lambda_k (-\psi_{-k}^2 + \psi_{+k}^2)$$

where  $k$  runs over all NOCV pairs. The deformation density plots provide insight into electron flow and the symmetry involved. In this work, charge flows from red regions ( $\Delta\rho_{\text{rho}} > 0$ ), to blue regions ( $\Delta\rho_{\text{rho}} < 0$ ).

## 3. Result and discussion

### 3.1. Structure and energy

Out of the thirty configurations examined, eighteen were confirmed as true minima, each featuring a central Si or Ge atom in a planar pentacoordinate environment. Exploration of the potential energy surface identified twelve global minima, distributed between six Si-centered structures in  $\text{SiE}_2\text{M}_3^{2+}$  and six Ge-centered structures in  $\text{GeE}_2\text{M}_3^{2+}$  (E = P, As; M = Ca, Sr, Ba). Fig. 2 shows some of the low-energy isomers, while the remaining isomers of each system are depicted in Fig. S1–S12. For systems with E = As, the second most stable isomer is between 2.1 and 5.1 kcal mol<sup>−1</sup> above the global minimum in  $\text{SiAs}_2\text{M}_3^{2+}$ , and between 0.1 and 2.2 kcal mol<sup>−1</sup> in  $\text{GeAs}_2\text{M}_3^{2+}$  (M = Ca, Sr,

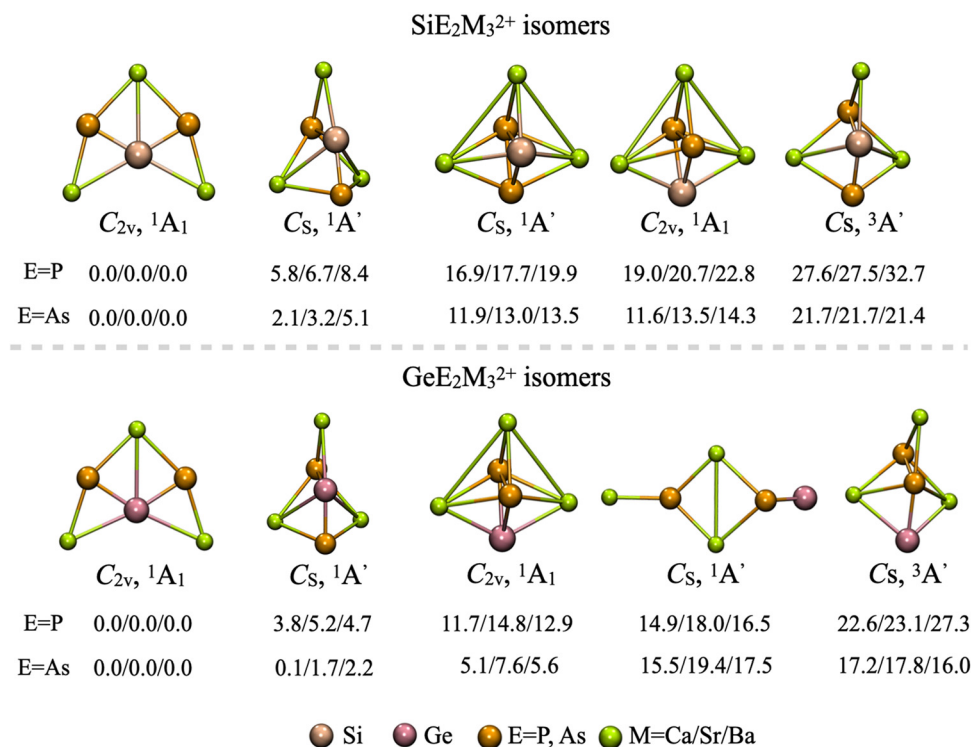


Fig. 2 Structures and relative energies in kcal mol<sup>−1</sup> of the low-energy isomers in  $\text{SiE}_2\text{M}_3^{2+}$  and  $\text{GeE}_2\text{M}_3^{2+}$  (E = P, As; M = Ca, Sr, Ba) computed at the CCSD(T)/aug-cc-pVTZ//PBE0-D3/aug-cc-pVTZ level of theory including ZPE corrections from PBE0-D3/aug-cc-pVTZ. Point group symmetries and spectroscopic states are indicated.

Ba). To ensure structural accuracy and confirm that these are true minima, additional optimizations and frequency analysis were performed at the MP2<sup>77</sup>/aug-cc-pVTZ level but only for the global minimum and the lowest energy local isomer, due to the small energy difference between them. The geometries obtained at the MP2 level are consistent with those optimized with PBE0-D3, with no significant differences in bond lengths or overall geometry.

Single-point energy calculations were performed on these structures at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory, and their values are shown in Fig. S13. Although the energy corrections obtained with CCSD(T)//MP2 are slightly larger than those calculated with CCSD(T)//PBE0-D3, both theoretical levels agree that the global minimum corresponds to a structure with a Si or Ge center in a planar pentacoordinate environment. The diagnostic  $T_1$  values for all global minima are below the 0.02 threshold, validating the use of a single-reference formalism and lending confidence to the accuracy of the computed energies at the CCSD(T) level. The triplet isomers ( $^3A'$  state,  $C_s$  symmetry), shown in the last column of Fig. 2, lie between 16 and 33 kcal mol<sup>-1</sup> above the singlet global minimum. Although some triplets present  $T_1$  values below 0.034, their high energy rules out that they compete in the relative stability of the system. Regarding the remaining six minima with Si and Ge centers in SiSb<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeSb<sub>2</sub>M<sub>3</sub><sup>2+</sup> (M = Ca, Sr, Ba), these correspond to local minima with energies 1.5 and 4 kcal mol<sup>-1</sup> above the global minimum, respectively (see Fig. S14–S19).

To evaluate the kinetic stability of the proposed systems, four representative global minima were selected in total, two with a Si center and two with a Ge center, from the SiE<sub>2</sub>Ca<sub>3</sub><sup>2+</sup> and GeE<sub>2</sub>Ca<sub>3</sub><sup>2+</sup> families with E being P and As. BOMD simulations were then performed at 298 and 600 K. Videos included in the SI show that the structures tend to maintain their planarity, with flexible motions of the Ca atoms around the SiE<sub>2</sub> and GeE<sub>2</sub> fragment. At 600 K, more pronounced thermal fluctuations are observed, particularly in the Ca atoms, which occasionally deviate from the plane without inducing structural rearrangements or isomerization processes. These results

support kinetic persistence at both room and moderately elevated temperatures.

All global minima of SiE<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeE<sub>2</sub>M<sub>3</sub><sup>2+</sup> (E = P, As; M = Ca, Sr, Ba) show that the Si/Ge–E distances remain constant as M increases and increase from P to As. Hereafter, the notation Si/Ge means “silicon or germanium”. The distances listed in Table 1 are shorter than the sums of the corresponding Pyykkö single-bond covalent radii (2.27 and 2.37 Å for Si–P and Si–As; 2.32 and 2.42 Å for Ge–P and Ge–As). Conversely, the Si/Ge–M<sub>1,2</sub> and Si/Ge–M<sub>3</sub> distances increase with the size of E and M. When compared to the Pyykkö covalent radii (2.87, 3.01 and 3.12 Å for Si–Ca, Si–Sr and Si–Ba; 2.92, 3.06 and 3.17 for Ge–Ca, Ge–Sr and Ge–Ba, respectively),<sup>78</sup> it is observed that the Si/Ge–M<sub>1,2</sub> distances are slightly larger, while for Si/Ge–M<sub>3</sub> they are longer but shorter than the sum of the van der Waals radii.<sup>79</sup>

Natural population analysis (NPA) reveals negative charges on the center Si/Ge and on E, balanced by positive charges on M<sub>1,2</sub> and M<sub>3</sub> (see Table 1). Generally, variations in the electronegativity of both E and the central atom influence the charge distribution: progressing from phosphorus (P) to arsenic (As) shifts electron density toward the central atom, whereas moving from Si to Ge directs charge density toward E. Notably, the charges on the metal sites (M) remain largely invariant across these changes.

The low WBI values for Si/Ge–M<sub>1,2</sub> (0.07–0.09) and Si/Ge–M<sub>3</sub> (0.003–0.005) indicated an insignificant covalent contribution (minimal overlap) with interactions dominated by electrostatic, whereas the high values for the Si/Ge–E (1.43–1.49) are consistent with strong two-center covalent bond. In line with the ppC systems reported by Leyva-Parra and co-workers, where C–E bonding is covalent and C–M interactions are weak and largely electrostatic, our Si/Ge-centered systems retain this pattern but the charge distribution changes: as C → Si → Ge, the center becomes less negative, E more negative, and M more positive. In addition, the Si/Ge–E bonds lengthen from P to As, and the Si/Ge–M interaction grows from Ca to Sr to Ba, while remaining weak and predominantly electrostatic.

According to the IUPAC coordination concept,<sup>80</sup> the observed arrangement, supported by interatomic distances,

**Table 1** HOMO–LUMO gap (gap, in eV), bond distances ( $r$ , Å), natural population analysis (NPA) charges ( $q$ , in |e|) and the Wiberg bond indices (WBIs) for the global minima in SiE<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeE<sub>2</sub>M<sub>3</sub><sup>2+</sup> (E = P, As and M = Ca, Sr, Ba) evaluated at the PBE0-D3/aug-cc-TZVP level

	PG	Gap	$r_{\text{Si}-\text{M}_{1,2}}$	$r_{\text{Si}-\text{M}_3}$	$r_{\text{Si}-\text{E}}$	$q(\text{Si})$	$q(\text{M}_{1,2})$	$q(\text{M}_3)$	$q(\text{E})$	WBI <sub>Si–M<sub>1,2</sub></sub>	WBI <sub>Si–M<sub>3</sub></sub>	WBI <sub>Si–E</sub>
SiP <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.46	2.87	3.01	2.18	–0.53	+1.70	+1.71	–1.30	0.093	0.003	1.48
SiP <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.23	3.03	3.19	2.18	–0.52	+1.74	+1.75	–1.35	0.069	0.003	1.49
SiP <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.31	3.20	3.38	2.18	–0.49	+1.74	+1.77	–1.38	0.071	0.003	1.48
SiAs <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.16	2.87	3.06	2.29	–0.73	+1.69	+1.70	–1.17	0.070	0.004	1.48
SiAs <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	2.95	3.04	3.26	2.29	–0.72	+1.73	+1.74	–1.24	0.070	0.004	1.49
SiAs <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.14	3.21	3.45	2.29	–0.68	+1.73	+1.75	–1.26	0.072	0.005	1.49
	PG	Gap	$r_{\text{Ge}-\text{M}_{1,2}}$	$r_{\text{Ge}-\text{M}_3}$	$r_{\text{Ge}-\text{E}}$	$q(\text{Ge})$	$q(\text{M}_{1,2})$	$q(\text{M}_3)$	$q(\text{E})$	WBI <sub>Ge–M<sub>1,2</sub></sub>	WBI <sub>Ge–M<sub>3</sub></sub>	WBI <sub>Ge–E</sub>
GeP <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.38	2.93	3.10	2.26	–0.50	+1.71	+1.71	–1.32	0.093	0.003	1.43
GeP <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.21	3.08	3.27	2.26	–0.50	+1.75	+1.75	–1.37	0.069	0.003	1.45
GeP <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.31	3.24	3.45	2.26	–0.46	+1.75	+1.77	–1.43	0.071	0.003	1.44
GeAs <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.17	2.93	3.15	2.37	–0.69	+1.70	+1.70	–1.20	0.070	0.004	1.44
GeAs <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	2.95	3.08	3.32	2.37	–0.69	+1.74	+1.74	–1.26	0.070	0.004	1.46
GeAs <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	C <sub>2v</sub>	3.05	3.26	3.52	2.37	–0.65	+1.73	+1.75	–1.29	0.072	0.005	1.45

NPA charges and WBI, fulfills the geometric criteria for planar pentacoordination at the central atoms. The nature and energetic contribution of the individual interactions are examined in detail in subsequent sections.

### 3.2. Chemical bond

AdNDP analysis, as an extension of the NBO approach, allows the recovery of lone pairs (LPs), classical 2c–2e bonds and multicenter delocalized bonds of the  $nc-2e$  type ( $n \geq 3$ ). In the global minima, one LP is recovered on each E (ON = 1.93–1.95 |e|) and one LP on Si/Ge oriented toward the metal-ring cavity (ON = 1.83–1.89 |e|). Two localized Si/Ge–E 2c–2e  $\sigma$  bonds with high occupancies (ON = 1.96–1.97 |e|) are also identified, together with a 3c–2e  $\sigma$  bond along the  $M_{1,2}$ –E– $M_3$  edge with a major contribution from E. In addition, two delocalized 3c–2e  $\pi$  bonds are recovered within the E–Si/Ge–E fragment: the first is concentrated mainly on the E atoms, exhibiting extended lone-pair character, while the second spans the entire E–Si/Ge–E fragment. The graphical representation is shown in Fig. 3a, and the corresponding occupation numbers (ON) are reported in Table S3. Both  $\pi$  distributions correspond to the canonical molecular orbitals (CMOs) HOMO and HOMO–3, respectively; their shapes are shown in Fig. 3b and their CMOs energies are listed in Table S4. No localized 2c–2e Si/Ge–M  $\sigma$  bond is recovered.

To probe the nature and strength of the interactions, energy decomposition analysis combined with natural orbitals for chemical valence (EDA–NOCV) was employed, using the Si/Ge center and the  $E_2M_3^{2+}$  ring as fragments. The total interaction energy ( $\Delta E_{\text{int}}$ ) ranges from –213.3 to –242.6 kcal mol<sup>–1</sup> and is more stabilizing for Si than for Ge and for P than for As. The orbital term ( $\Delta E_{\text{orb}}$ ) dominates the stabilization and contributes between 64 and 70% of the attractive interaction. The electrostatic

Table 2 EDA result of the Si (S, 3s<sup>2</sup>3p<sup>2</sup>) or Ge (S, 4s<sup>2</sup>4p<sup>2</sup>) +  $E_2M_3^{2+}$  (S) as interacting fragments at the PBE0–D3/TZ2P–ZORA//PBE0–D3/aug-cc-pVTZ level. All energy values are in kcal mol<sup>–1</sup>

System	$\Delta E_{\text{orb}}$	$\Delta E_{\text{elstat}}$	$\Delta E_{\text{disp}}$	$\Delta E_{\text{Pauli}}$	$\Delta E_{\text{int}}$	% $\Delta E_{\text{orb}}$	% $\Delta E_{\text{elstat}}$
SiP <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	–812.6	–358.1	0.2	929.2	–241.3	69	31
SiP <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	–806.6	–353.4	0.2	917.2	–242.6	70	30
SiP <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	–786.9	–348.8	0.6	895.1	–240.1	69	31
SiAs <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	–754.4	–361.4	0.0	884.5	–231.3	68	32
SiAs <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	–744.2	–353.8	0.0	866.3	–231.8	68	32
SiAs <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	–725.8	–347.8	0.3	844.0	–229.3	68	32
GeP <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	–712.8	–363.4	0.2	855.6	–220.6	66	34
GeP <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	–712.3	–362.7	0.3	852.6	–222.1	66	34
GeP <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	–699.5	–359.9	0.7	837.9	–220.7	66	34
GeAs <sub>2</sub> Ca <sub>3</sub> <sup>2+</sup>	–671.6	–369.8	0.0	828.2	–213.3	64	36
GeAs <sub>2</sub> Sr <sub>3</sub> <sup>2+</sup>	–666.7	–365.4	0.1	817.9	–214.1	65	35
GeAs <sub>2</sub> Ba <sub>3</sub> <sup>2+</sup>	–653.7	–360.6	0.5	801.3	–212.5	64	36

term ( $\Delta E_{\text{elstat}}$ ) accounts for between 30 and 36%, whereas dispersion ( $\Delta E_{\text{disp}}$ ) is minor. Pauli repulsion ( $\Delta E_{\text{Pauli}}$ ) tends to decrease along the series Si → Ge, P → As and Ca → Sr → Ba, consistent with more diffuse electron clouds in heavier atoms leading to reduced steric repulsion. Overall, lighter centers (Si) and pnictogens (P) enhance the orbital (covalent) component, while Si → Ge or P → As substitutions modestly increase electrostatic character; the effect of M (Ca → Sr → Ba) is minor (see Table 2).

Decomposition of  $\Delta E_{\text{orb}}$  into NOCV pairs (Fig. 4, shown for the representative SiP<sub>2</sub>Ca<sub>3</sub><sup>2+</sup>) yields four homologous contributions across the series. The first NOCV (~40% of  $\Delta E_{\text{orb}}$ ) represents a  $\sigma$ -bond between the s-orbital of the central atom and a  $\pi$ -orbital from the ring (mainly E atoms). The second (~20%) corresponds to a  $\pi$ -orbital reorganization in both fragments, and the third (~20%) to  $\pi$ -cloud formation *via* intrafragment reorganization. Together they recover ~80% of  $\Delta E_{\text{orb}}$ . The fourth NOCV represents a center-ring

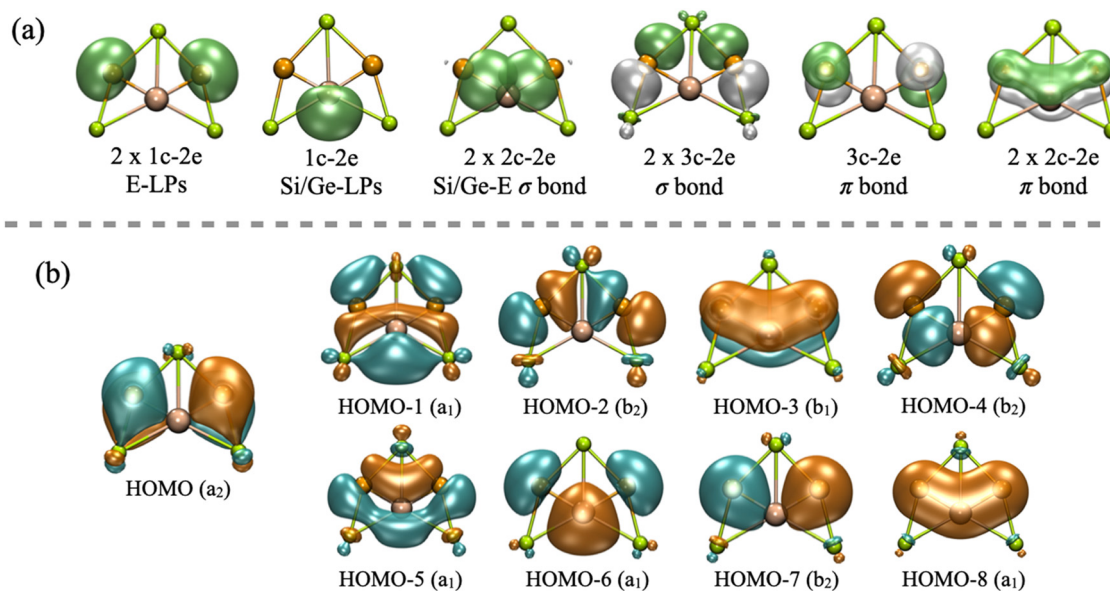


Fig. 3 Graphical representation of (a) bonding pattern from AdNDP analysis, calculated for the global minima ppSi and ppGe in SiE<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeE<sub>2</sub>M<sub>3</sub><sup>2+</sup> (E = P, As; M = Ca, Sr, Ba) at the PBE0–D3/aug-cc-pVTZ level and (b) canonical molecular orbitals (CMOs).

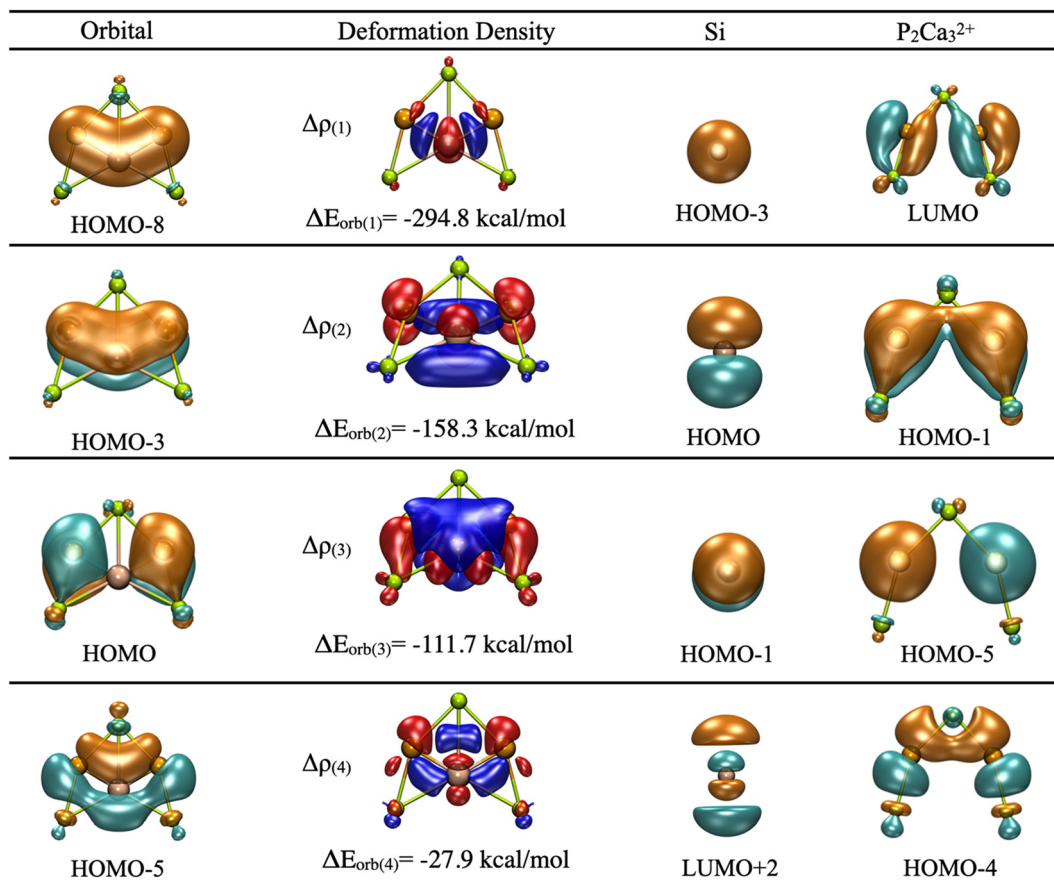


Fig. 4 Plot of the deformation densities,  $\Delta\rho_{(1)-(4)}$  corresponding to  $\Delta E_{\text{orb}(1)-(4)}$  and the related interacting orbitals of the fragments in the  $\text{SiP}_2\text{Ca}_3^{2+}$  system at the PBE0-D3/TZ2P-ZORA level. The charge flow of the deformation densities is from red to blue. The isovalue for  $\Delta\rho_{(1)}$  and  $\Delta\rho_{(2)}$  is 0.001 a.u. and for the rest is 0.0005 a.u.

electron-density reorganization rather than an independent

Polarization increases from Si to Ge but does not develop into a distinct two-center  $\sigma$  bond.

**Table 3** Energy components of IQA (in  $\text{kcal mol}^{-1}$ ) between atom pairs in of  $\text{TtE}_2\text{M}_3^{2+}$  (Tt = Si, Ge; E = P, As; M = Ca, Sr, Ba) at PBE0-D3/aug-cc-pVTZ level.  $\Delta E_{\text{IOA}}$  represents the integration error. The reported values include the total interatomic interaction energy, the Coulomb component, and the exchange–correlation component

	$\text{SiP}_2\text{Ca}_3^{2+}$	$\text{SiP}_2\text{Sr}_3^{2+}$	$\text{SiP}_2\text{Ba}_3^{2+}$	$\text{SiAs}_2\text{Ca}_3^{2+}$	$\text{SiAs}_2\text{Sr}_3^{2+}$	$\text{SiAs}_2\text{Ba}_3^{2+}$	$\text{GeP}_2\text{Ca}_3^{2+}$	$\text{GeP}_2\text{Sr}_3^{2+}$	$\text{GeP}_2\text{Ba}_3^{2+}$	$\text{GeAs}_2\text{Ca}_3^{2+}$	$\text{GeAs}_2\text{Sr}_3^{2+}$	$\text{GeAs}_2\text{Ba}_3^{2+}$
$\Delta E_{\text{IOA}}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$V_{\text{IOA}}^{\text{int}}(\text{Tt} - \text{E})$	-436.1	-439.1	-439.4	-224.6	-230.3	-243.0	-173.7	-173.7	-180.0	-130.7	-131.6	-139.6
$V_{\text{C}}^{\text{int}}(\text{Tt} - \text{E})$	-282.2	-285.5	-289.2	-59.9	-66.5	-83.6	-4.7	-4.2	-13.6	31.8	30.9	19.8
$V_{\text{XC}}^{\text{int}}(\text{Tt} - \text{E})$	-153.9	-153.6	-150.2	-164.7	-163.8	-159.4	-169.0	-169.5	-166.4	-162.5	-162.5	-159.4
$V_{\text{IOA}}^{\text{int}}(\text{Tt}-\text{M}_{1,2})$	63.2	60.5	64.7	-41.9	-37.2	-19.0	-58.8	-60.2	-45.4	-99.2	-96.2	-76.7
$V_{\text{C}}^{\text{int}}(\text{Tt}-\text{M}_{1,2})$	86.4	83.8	89.5	-15.4	-11.2	8.2	-36.2	-37.3	-20.9	-74.3	-71.5	-50.5
$V_{\text{XC}}^{\text{int}}(\text{Tt}-\text{M}_{1,2})$	-23.2	-23.3	-24.8	-26.5	-26.0	-27.3	-22.6	-22.9	-24.5	-25.0	-24.7	-26.2
$V_{\text{IOA}}^{\text{int}}(\text{Tt}-\text{M}_3)$	162.5	157.1	149.5	45.3	47.8	54.8	8.9	7.8	13.7	-33.8	-31.0	-20.1
$V_{\text{C}}^{\text{int}}(\text{Tt}-\text{M}_{1,2})$	168.6	162.6	155.6	53.8	55.3	62.8	17.0	15.4	22.1	-24.6	-22.6	-11.0
$V_{\text{XC}}^{\text{int}}(\text{Tt}-\text{M}_{1,2})$	-6.1	-5.5	-6.1	-8.5	-7.5	-7.9	-8.1	-7.6	-8.4	-9.2	-8.4	-9.1
$V_{\text{IOA}}^{\text{int}}(\text{E}-\text{M}_{1,2})$	-379.6	-373.9	-344.2	-301.3	-299.8	-278.6	-302.4	-298.7	-275.9	-262.8	-261.1	-241.6
$V_{\text{C}}^{\text{int}}(\text{E}-\text{M}_{1,2})$	-315.9	-313.0	-274.5	-242.2	-242.7	-213.3	-238.7	-238.2	-206.9	-202.9	-203.6	-176.1
$V_{\text{XC}}^{\text{int}}(\text{E}-\text{M}_{1,2})$	-63.7	-60.9	-69.7	-59.1	-57.1	-65.3	-63.7	-60.5	-69.1	-59.9	-57.5	-65.5
$V_{\text{IOA}}^{\text{int}}(\text{E}-\text{M}_3)$	-346.4	-314.4	-312.2	-275.0	-273.6	-251.8	-270.2	-267.5	-244.8	-235.6	-234.6	-214.3
$V_{\text{C}}^{\text{int}}(\text{E}-\text{M}_{1,2})$	-301.6	-297.5	-263.3	-232.4	-231.6	-205.2	-225.9	-224.0	-196.5	-193.0	-192.6	-167.8
$V_{\text{XC}}^{\text{int}}(\text{E}-\text{M}_{1,2})$	-44.8	-43.9	-48.9	-42.6	-42.0	-46.6	-44.3	-43.5	-48.3	-42.5	-42.0	-46.5

These findings again raise the question of what interaction links the Si/Ge center to M. To complement EDA–NOCV and apply an energy-based interatomic criterion, we next employ the Interacting Quantum the Atoms (IQA) framework. Table 3 summarizes the interatomic components for representative Tt–E, Tt–M<sub>1,2</sub>, and Tt–M<sub>3</sub> pairs (Tt = Si or Ge). Across all global minima, Tt–E interactions are attractive and typically display a comparatively large  $V_{XC}$ , except for the SiP<sub>2</sub>M<sub>3</sub><sup>2+</sup> series, where Si–P is predominantly  $V_C$ . Planar pentacoordination arises only when all five interactions (two Tt–E and three Tt–M) are attractive in IQA, a condition met only by GeAs<sub>2</sub>M<sub>3</sub><sup>2+</sup>, whose Ge–M interactions are largely Coulombic. By contrast, Tt–M behavior depends on both the pnictogen and the metal: in SiP<sub>2</sub>M<sub>3</sub><sup>2+</sup>, Si–M<sub>1,2</sub> and Si–M<sub>3</sub> are repulsive (dicoordination); in SiAs<sub>2</sub>M<sub>3</sub><sup>2+</sup>, Si–M<sub>1,2</sub> becomes attractive with  $V_{XC} > V_C$  while Si–M<sub>3</sub> remains repulsive (tetracoordination); in GeP<sub>2</sub>M<sub>3</sub><sup>2+</sup>, Ge–M<sub>1,2</sub> is attractive with  $V_C > V_{XC}$  for light metals and shifts toward larger  $V_{XC}$  as M becomes heavier, whereas Ge–M<sub>3</sub> remains repulsive (tetracoordination); in GeAs<sub>2</sub>M<sub>3</sub><sup>2+</sup>, all three Ge–M interactions are attractive and predominantly Coulombic. Thus, IQA analysis shows that the specific Ge–M interactions enabling genuine pentacoordination are chiefly electrostatic, which reconciles the strong global orbital stabilization found by EDA–NOCV with the absence of a localized Tt–M two-center  $\sigma$  bond.

Even when true planar pentacoordination at the center is not achieved, the structure remains bound because the E–M<sub>1,2</sub> and E–M<sub>3</sub> interatomic interactions, attractive and predominantly Coulombic, compensate for the lack of bonding between the center and some metals, thereby sustaining the planar geometry.

## 4. Conclusions

Guided by the 18-valence-electron (18ve) design principle, twelve  $C_{2v}$ -symmetric global minima were identified for the SiE<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeE<sub>2</sub>M<sub>3</sub><sup>2+</sup> systems (E = P, As; M = Ca, Sr, Ba). Their stability was assessed through potential energy surface (PES) exploration and Born–Oppenheimer molecular dynamics (BOMD) simulations at 298 and 600 K. According to the IUPAC coordination concept, all identified minima satisfy the geometric criteria for planar pentacoordination at the silicon and germanium centers. Energy decomposition analysis combined with natural orbitals for chemical valence (EDA–NOCV) indicates that orbital interactions ( $\Delta E_{orb}$ ) contribute predominantly to the stabilization, primarily *via*  $\sigma$  coupling between the central *s* orbital of Si/Ge and the  $\pi$  system of the E<sub>2</sub>M<sub>3</sub><sup>2+</sup> ring. The three principal NOCV pairs account for approximately 80% of  $\Delta E_{orb}$ , dominated by this  $\sigma$  s(Si/Ge)– $\pi$ (ring) interaction, along with two  $\pi$  orbital reorganizations. A fourth NOCV pair corresponds to center–ring polarization and does not represent an independent two-center Si/Ge–M  $\sigma$  bond. Using the interacting quantum atoms (IQA) approach as an energy-based interatomic criterion, distinctions are made between systems that are only geometrically pentacoordinate and those that are

energetically tetra- or dicoordinate. In SiP<sub>2</sub>M<sub>3</sub><sup>2+</sup> species, all three Si–M interactions are repulsive, consistent with planar dicoordination. In SiAs<sub>2</sub>M<sub>3</sub><sup>2+</sup> and GeP<sub>2</sub>M<sub>3</sub><sup>2+</sup>, the interaction of the center with one of the metals is not attractive, suggesting of planar tetracoordination. Only GeAs<sub>2</sub>M<sub>3</sub><sup>2+</sup> exhibits genuine planar pentacoordination, with attractive and predominantly Coulombic Ge–M interactions, while Ge–E interactions are attractive with a significant exchange–correlation covalent contribution. This analysis suggests that peripheral E–M interactions contribute to maintaining the planar geometry even in the absence of a localized Si/Ge–M bond and that the global minimum of GeAs<sub>2</sub>M<sub>3</sub><sup>2+</sup> exhibits a ppGe, consistent with the 18ve rule.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data supporting this article are provided in the supplementary information (SI). The supplementary information (SI) contains relevant data supporting this study, including Cartesian coordinates of the investigated clusters, comprehensive AdNDP representations, and molecular dynamics simulation videos. See DOI: <https://doi.org/10.1039/d5cp03108g>.

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