



Cite this: *Phys. Chem. Chem. Phys.*, 2025, 27, 23468

# Tunable reducibility of alkaline earth metal clusters for carbon dioxide and nitrogen molecule activation: a QM-QSPR study

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A hybrid approach combining *ab initio* computational techniques of quantum chemistry with a machine learning strategy was used to design and investigate  $\text{BAe}_3$  (Ae = Be, Mg, Ca, Sr, and Ba) molecular clusters with strong reducing abilities. In these systems, the type of electropositive alkaline earth metal atoms was varied to tune the physicochemical properties of the resulting  $\text{BAe}_3$  system. Both basic systems (built of three identical substituents, such as  $\text{BSr}_3$ ) and mixed systems (containing various substituents, such as  $\text{BCaMg}_2$ ) were considered. The  $\text{BAe}_3$  clusters feature low ionization energies (IEs) and a highly delocalized singly occupied molecular orbital (SOMO). Among them, the  $\text{BBa}_3$  cluster was identified as having the lowest IE here (3.82 eV), exhibiting the superalkali characteristic, which is smaller than that of any alkali [3.89 eV (cesium atom)]. The  $\text{BAe}_3^+$  thermodynamically stable closed-shell cations were shown to accommodate two electrons into their Rydberg orbitals, forming the double-Rydberg anions with electron binding energies in the 0.434–1.988 eV range. A mathematical model describing the dependence of IEs of  $\text{BAe}_3$  clusters on their composition was developed. Different from the conventional formulation-assisted methodology, the quantitative structure–property relationship (QSPR) strategy predicts the reducing ability of a  $\text{BAe}_3$  superalkali, where a suitable alkaline earth metal decreases the IE of the resulting  $\text{BAe}_3$  cluster via the B–Ae and Ae–Ae electrostatic effects. Finally, the potential application of  $\text{BAe}_3$  electron donors in the reduction of counterpart systems with low electron affinity (such as carbon dioxide or nitrogen molecules) was demonstrated. From the analysis of the binding energy between  $\text{BAe}_3$  and the Y (Y =  $\text{CO}_2$  and  $\text{N}_2$ ) counterparts, as well as the charge transfer, and the geometry of  $\text{BAe}_3/\text{Y}$  systems, it follows that the resulting structures can be considered as either the  $[\text{BAe}_3/\text{Y}]$  complexes or the  $\text{BAe}_3\text{Y}$  compounds. It is shown that the IE and the dipole moment of  $\text{BAe}_3$  determine the stability and geometry of the resulting  $\text{BAe}_3/\text{Y}$  species. The lower IE and larger dipole moment promote the reactivity of  $\text{BAe}_3$  and result in the formation of stable, strongly bound compounds. These findings highlight how the structure and stability of the  $\text{BAe}_3/\text{Y}$  systems can be tuned upon single atom substitution and can be used to bond and remove toxic molecules from the environment.

Received 30th July 2025,  
 Accepted 23rd September 2025

DOI: 10.1039/d5cp02913a

rs.c.li/pccp

## 1. Introduction

Reducing agents play a crucial part in chemical synthesis.<sup>1,2</sup> Strong reductors have low ionization energies. Among the periodic table elements, alkali metal atoms exhibit the lowest ionization energies (5.39–3.89 eV). Superalkalis have even lower ionization energies than those of the alkali metal atoms. In 1982, Gutsev and Boldyrev introduced the simple formula  $\text{ML}_{k+1}$  to describe one class of superalkalis, where M is a  $k$ -valent electronegative central atom ligated with  $k + 1$  alkali-metal

atoms (L).<sup>3</sup> Typical examples of such superalkalis are  $\text{FLi}_2$ ,<sup>4,5</sup>  $\text{OLi}_3$ ,<sup>6,7</sup> and  $\text{CLi}_5$ .<sup>8</sup> The  $\text{ML}_{k+1}$  molecular system exhibits a high tendency to lose one valence electron, forming a very stable cation with the positive charges distributed over all the  $k + 1$  alkali atoms (L). The existence of  $\text{OL}_3$  (L = Li, Na, and K),  $\text{ML}_2$  (M = F, Cl, Br, and I; L = Li, Na, and K),  $\text{SLi}_3$ ,  $\text{Li}_3\text{F}_2$ ,  $\text{Li}_2\text{CN}$ , and  $\text{Na}_2\text{CN}$  superalkalis has been confirmed by experiments.<sup>9</sup> Since the early 1980s, a lot of effort has been devoted to proposing alternative superalkali species, including polynuclear  $\text{N}_4\text{Mg}_6\text{L}$  (M = Li, Na, and K) superalkali species, alkali-metal coordinated crown ether complexes,<sup>10</sup> organic heterocyclic molecules,<sup>11</sup> superalkali molecules containing halogenoids,<sup>12,13</sup> organo-Zintl superalkalis,<sup>14</sup> and superalkalis with a boron atom acting as the central atom.<sup>15,16</sup> Despite these achievements, it is still desirable to obtain novel superalkali species, to seek even lower

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ionization energies. The boron-based superalkali design seems to be the most promising direction to obtain efficient reducers for CO<sub>2</sub> and N<sub>2</sub> activation.

Exploration of new superalkali species aims to provide reliable data and predictions of the use of such compounds as electron donors in the reduction of counterpart systems with low electron affinity, as well as the role they can play more generally in materials science.<sup>1</sup> The low ionization energies of superalkalis make them candidates for catalysts for N<sub>2</sub> and CO<sub>2</sub> conversion into ammonia and fuel, respectively.<sup>17–20</sup> By using the superalkalis as building blocks of cluster-assembled materials, we can achieve the functional features of atom-based materials (like conductivity or catalytic potential) while having more flexibility to achieve higher performance.<sup>21–25</sup> Superalkalis could be substituted for atoms as functional units because they potentially possess atomic-like functions (including redox activity).<sup>1,22</sup> To date, only a few superalkali-based bulk materials have been synthesized.<sup>26,27</sup>

Small isolated molecular clusters can serve as catalytic centres in single-cluster catalysis. In single-cluster catalysis, the metal clusters are not aggregated into larger particles or bulk materials, but rather, they exist as isolated entities, often stabilized on a support material (such as oxide or carbon supports). For instance, the triatomic ruthenic cluster supported by carbon nitride species (Ru<sub>3</sub>/CN) has shown outstanding performance in the selective oxidation reaction of alcohols to aldehydes.<sup>28</sup> However, the controlled synthesis of supported atomic clusters is challenging, as stabilizing the precise numbers of atoms on the support in a rational manner is difficult. The synthetic methods to prepare supported metal clusters with precise numbers of atoms include a precursor-preselected approach,<sup>28</sup> host-guest strategy,<sup>29</sup> wet chemical reduction,<sup>30</sup> dendrimer-based technique,<sup>31</sup> and atomic layer deposition method.<sup>32,33</sup> The size of molecular clusters determines the fraction of surface atoms, which has a significant effect on both catalytic activity and selectivity. In supported atomic clusters, most of the metal atoms are exposed and available for the reactant molecules. As a result, supported atomic clusters exhibit much higher utilization efficiency in catalytic reactions compared to corresponding nanoparticles or single-atom catalysts.<sup>33</sup> Supported atomic clusters also possess unique electronic structures due to the orbital overlapping between metal atoms. The synergistic effect among metal atoms for boosting catalytic performances is uniquely distinct in supported atomic clusters containing two or more types of metal atoms.<sup>34</sup> With the development of synthesis and characterization, supported atomic clusters are expected to become a key area of research. Since the composition and structure of superalkali clusters can be tuned to optimize the selectivity and efficiency of the catalyst, designing and investigating this class of compounds for single-cluster catalysis applications holds great promise.

This contribution is aimed at designing superalkalis for redox applications and as building blocks for cluster-assembled materials. According to our recent results,<sup>17</sup> a superalkali with lower ionization energy should more easily transfer an electron to counterpart molecules (*e.g.*, carbon dioxide or nitrogen) compared to one with higher ionization energy. A promising direction for

designing effective reducers is by utilizing boron-based molecules (such as BCa<sub>3</sub><sup>35</sup> or BLi<sub>6</sub><sup>4</sup>). Boron atoms have both empty and occupied atomic orbitals (in resemblance to the d orbitals of the gold atom<sup>21</sup>), which makes them capable of synergistically accepting and donating electrons. Thus, we decided to consider novel superalkali systems utilizing boron-based molecules. Specifically, our candidates were BAe<sub>3</sub> clusters (Ae = Be, Mg, Ca, Sr, and Ba). In these systems, we can change the type of electro-positive atoms to tune the physicochemical properties of the resulting system. There are both basic (built of the identical three substituents, such as B Sr<sub>3</sub>) and mixed (containing various substituents, such as B CaMg<sub>2</sub>) systems. Since alkaline earth elements (Mg, Ca, Sr, and Ba) are abundant and cheap,<sup>36,37</sup> using them to facilitate industrially relevant chemical transformations is prospective. Recently, we used alkaline earth metal atoms in superalkali design and proved that they can donate valence electrons to the central atom.<sup>17</sup> By using diverse alkaline earth metal ligands decorating the central boron atom, we were able to design superatoms with the desired ionization energy values. The studied superatomic systems with high thermodynamic stability and low ionization energy can act as reducing agents of carbon dioxide and nitrogen molecules.

## 2. Theoretical methods

### 2.1. Quantum chemistry methods

The second-order Møller-Plesset (MP2) perturbational method was employed with the Pople split-valence basis sets of triple zeta quality, 6-311+G(3df),<sup>38</sup> to optimize the geometry of BAe<sub>3</sub><sup>0/±</sup> (M = Be, Mg, Ca, Sr, and Ba) and BAe<sub>3</sub>/Y (Y = CO<sub>2</sub> and N<sub>2</sub>) ground states. For the relaxed structures, the vibrational frequencies were obtained at the same level of theory. The coupled-cluster method with single, double, and non-iterative triple excitations, CCSD(T), using the 6-311+G(3df) basis, was applied to estimate the final energies of the species at their MP2/6-311+G(3df) equilibrium geometries. The basis sets of Ahlrichs and coworkers' split valence and quadrupole zeta quality (Def2TZVP) were employed for strontium and barium atoms.<sup>39,40</sup> The above computations were carried out using the Gaussian 16 (Rev. C.01) software.<sup>41</sup>

In the next step, the reducing (ionization energy) and oxidizing (electron affinity) abilities of non-mixed and mixed BAe<sub>3</sub> (Ae = Be, Mg, Ca, Sr, and Ba) molecular clusters were evaluated. The adiabatic ionization energy (AIE) was estimated by subtracting the total electronic energies of the cation ( $E_{\text{cat}}$ ) and neutral species ( $E_{\text{neu}}$ ) at each equilibrium geometry ( $r_{e,+}$  and  $r_{e,0}$ , respectively; eqn (1)). The adiabatic electron affinity (AEA) was calculated by subtracting the total electronic energies of the neutral ( $E_{\text{neu}}$ ) and anionic species ( $E_{\text{an}}$ ) at each equilibrium geometry ( $r_{e,0}$  and  $r_{e,-}$ , respectively; eqn (2)). The vertical ionization energy (VIE, eqn (3)) and the vertical electron affinity (VEA, eqn (4)) values were obtained at the CCSD(T)/6-311+G(3df) level of theory at the MP2/6-311+G(3df) equilibrium geometries of the neutral species ( $r_{e,0}$ ).

$$\text{AIE} = E_{\text{cat}}(r_{e,+}) - E_{\text{neu}}(r_{e,0}) \quad (1)$$

$$\text{AEA} = E_{\text{neu}}(r_{e,0}) - E_{\text{an}}(r_{e,-}) \quad (2)$$



$$\text{VIE} = E_{\text{cat}}(r_{e,0}) - E_{\text{neu}}(r_{e,0}) \quad (3)$$

$$\text{VEA} = E_{\text{neu}}(r_{e,0}) - E_{\text{an}}(r_{e,0}) \quad (4)$$

The adiabatic ionization energies (AIEs) and vertical electron affinities (AEAs) were calculated using the CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df) approach and comprising zero-point energy corrections. The stabilities of  $\text{BAe}_3^{0/\pm}$  systems were examined by obtaining their binding energies per atom ( $E_b$ ) at the CCSD(T)/6-311+G(3df)+Def2QZVP level, defined as given in the following equations:

$$E_b(\text{BAe}_3) = \frac{[E(\text{B}) + 3 \cdot E(\text{Ae}) - E(\text{BAe}_3)]}{4} \quad (5)$$

$$E_b(\text{BAe}_3^+) = \frac{[E(\text{B}) + 2 \cdot E(\text{Ae}) + E(\text{Ae}^+) - E(\text{BAe}_3^+)]}{4} \quad (6)$$

$$E_b(\text{BAe}_3^-) = \frac{[E(\text{B}^-) + 3 \cdot E(\text{Ae}) - E(\text{BAe}_3^-)]}{4} \quad (7)$$

The binding energy (BE) values of the superalkali/Y systems (Y =  $\text{CO}_2$  and  $\text{N}_2$ ) were estimated at the CCSD(T)/6-311+G(3df)+Def2QZVP level of theory, eqn (8).

$$\text{BE} = E_{\text{superalkali/Y}} - E_{\text{superalkali}} - E_Y \quad (8)$$

The Multiwfn v.3.6 program was used for wavefunction analyses.<sup>42,43</sup> The frontier molecular orbitals were generated with the ChemCraft v.1.8 program,<sup>44</sup> and the contour values used in the plots were estimated with the OpenCubeMan rev.0.01<sup>45</sup> using a fraction of electron density equal to 0.8.

## 2.2. Quantitative structure–property relationship (QSPR) modeling

The designed  $\text{BAe}_3$  clusters were split into a training set used for calibrating a QSPR model and a test set later used for evaluating the predictive ability of the developed QSPR equation. The QSPR modeling was performed following the recommendations by the Organization for Economic Co-operation and Development (OECD). In the OECD principles for the structure–property relationship approach, the accurately developed and validated model should meet the following five conditions: (i) a defined endpoint, (ii) an unambiguous algorithm, (iii) a defined applicability domain (AD), (iv) appropriate measures of goodness-of-fit, robustness, and predictivity and (v) a mechanistic interpretation, if possible.<sup>46,47</sup> The OECD principles are fulfilled by the developed QSPR model since it has a clearly described endpoint (adiabatic ionization energy) and the algorithm (a simple linear regression, SLR). In the SLR approach, the endpoint ( $y_i$ ) is defined as the linear regression model of the most relevant descriptor used as a variable ( $x$ , eqn (9)):

$$y_i = b_0 + b_1 \cdot x \quad (9)$$

The next essential step of the model's development was to define its applicability domain. The applicability domain is a theoretical region restricted by the range of the endpoint and structural similarity between the compounds of interest, whereas the model predictions are the most reliable. In the

present study, the structural applicability domain was verified by the leverage approach. The leverage values ( $h_i$ ) were obtained as follows (eqn (10)):<sup>48</sup>

$$h_i = x_i^T (X^T X)^{-1} x_i \quad (i = 1, \dots, n) \quad (10)$$

where  $x_i$  stands for the descriptor row-vector of the  $i$ th molecular cluster,  $x_i^T$  is the transpose of  $x_i$ ,  $X$  is the descriptor matrix, and  $X^T$  is the transpose of  $X$  matrix. In the leverage approach, the critical leverage ( $h^*$ ) is fixed at  $3(m+1)/n$  value, where  $n$  represents the number of compounds in the training set and  $m$  is the number of descriptors engaged in the correlation. The model's prediction is unreliable for a molecule whose leverage ( $h_i$ ) exceeds the critical  $h^*$  value.<sup>47</sup> In contrast, when the leverage value of a compound is lower than the critical  $h^*$  value, the probability of accuracy between predicted and observed (experimental) values is as high as that for the compounds in the training set. The possibility of a compound being within the QSPR model's structural applicability domain can be verified for each new compound, and the only knowledge needed is the molecular structure information represented by the molecular descriptors selected in the QSPR model.

In the last step, the developed QSPR was validated by both internal and external validation. For the internal validation, the leave-one-out cross-validation method (LOO) was employed, and the model's robustness was assessed by the cross-validation coefficient ( $Q_{CV}^2$ ) and the root mean square of cross-validation ( $\text{RMSE}_{CV}$ ). The external validation of the model was conducted with an external test set composed of data not used to develop the prediction QSPR equation. The predictive ability of the model was defined by the external validation coefficient ( $Q_{EXT}^2$ ) and the root mean square of prediction ( $\text{RMSE}_{EXT}$ ). Statistics describing goodness-of-fit, robustness, and prediction ability of the QSPR model were obtained with the equations presented in Table S9.

## 3. Results

### 3.1. Geometry and thermodynamic stability of non-mixed and mixed $\text{BAe}_3$ clusters

We first optimized the lowest-energy structures of the non-mixed  $\text{BAe}_3^{0/\pm}$  (Ae = Be, Mg, Ca, Sr, and Ba) clusters (Fig. 1 and 2), from which the adiabatic ionization energies of  $\text{BAe}_3$  were estimated to be in the 3.818–6.830 eV range, exhibiting an alkali-like characteristic. As shown in Fig. 1 and 2, in the neutral non-mixed  $\text{BAe}_3$  (Ae = Be, Mg, Ca, Sr, and Ba) clusters, the B central atom binds with three Ae substituents forming a pyramidal geometry of the  $C_{3v}$ -symmetry with the dihedral B–Ae<sub>1</sub>–Ae<sub>2</sub>–Ae<sub>3</sub> angle in the 39–65° range and decreases with an increase in the atomic radii of alkaline earth metal atoms. These findings are consistent with a previous study on triligated boron species,<sup>35</sup> validating the accuracy of the present theoretical level. Also, we found out that replacing Pople's split-valence triple-zeta basis set with standard sets of diffuse and polarization functions, 6-311+G(d), supplemented by three d-symmetry sets plus one f-symmetry set of polarization (*i.e.*, 6-311+G(3df)) leads to significantly better electronic stability estimation (Table S1 of the SI).



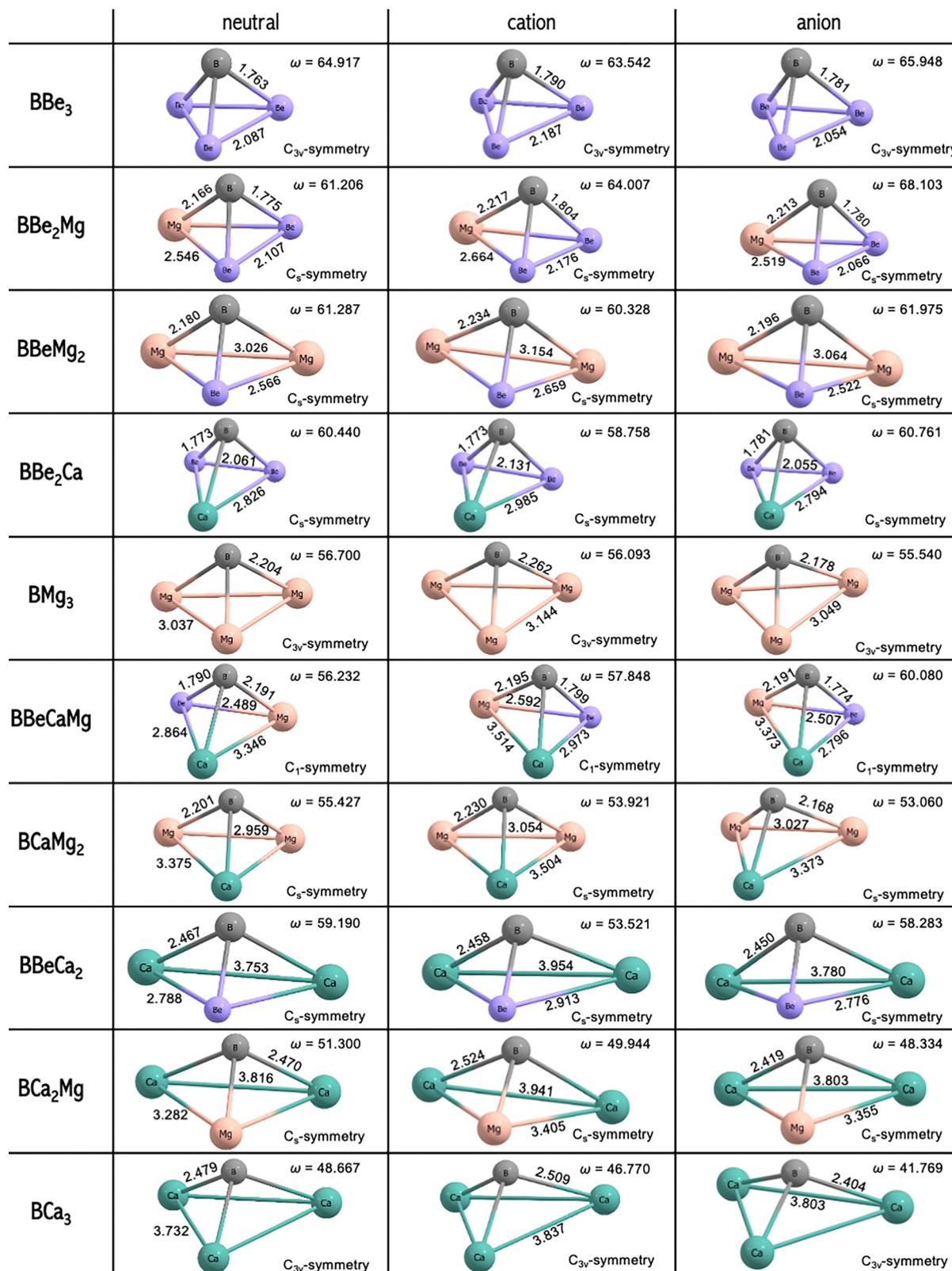


Fig. 1 The MP2(full)/6-311+G(3df) ground state structures of  $BAe_3^{0/\pm}$  ( $Ae = Be, Mg, \text{ and } Ca$ ) species. Bond lengths in Å and dihedral  $B-Ae_1-Ae_2-Ae_3$  angles ( $\omega$ ) in degrees. See Section S1 in the SI for higher energy isomers.



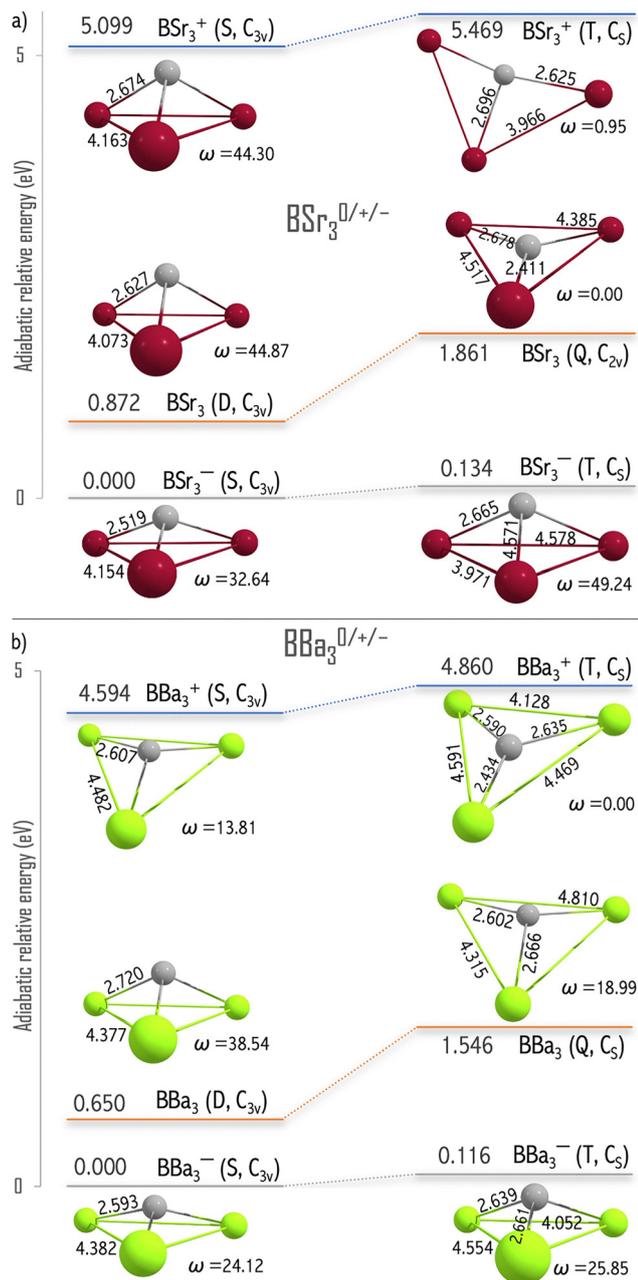


Fig. 2 The CCSD(T)/full/6-311+G(3df)+Def2TZVP//MP2(full)/6-311+G(3df)+Def2TZVP energy diagrams showing adiabatic relative stability of (a)  $\text{BSr}_3^{0/\pm}$  and (b)  $\text{BBa}_3^{0/\pm}$  close- [singlet (S)] and open-shell [doublet (D), triplet (T), quartet (Q)] systems (with respect to the corresponding lowest energy anionic  $\text{BAe}_3^-$  singlet spin states, whose energies were taken as zero). Bond lengths in Å and dihedral B–Ae<sub>1</sub>–Ae<sub>2</sub>–Ae<sub>3</sub> angles ( $\omega$ ) in degrees.

A similar tendency was found in the case of another class of superatoms, superhalogens, where the performance of the MP2/6-311+(3df) and CCSD(T)/6-311+(3df) approaches assures a very high accuracy of the results (the deviations should not exceed 3%).<sup>49</sup>

The  $\text{BAe}_3$  systems are thermodynamically stable due to electrostatic interaction between the electron-withdrawing boron atom and electropositive alkaline earth metals (electronegativity in the Pauling scale in the 0.89–1.57 eV range) as well

as covalent-like interactions between alkaline earth atoms. The Be–Be (2.09 Å), Mg–Mg (3.04 Å), Ca–Ca (3.72 Å), Sr–Sr (4.07 Å), and Ba–Ba (4.38 Å) bonds of non-mixed  $\text{BAe}_3$  clusters are near the bond lengths of homometallic bonding of  $\text{M}_2^{2+}$  cations (2.14, 2.91, 3.74, 4.23, and 4.69 Å respectively, as obtained at the same level of theory). The positive Gibbs free energies of the most probable dissociation channels (Table 1 and Table S2) and the non-mixed  $\text{B}_2\text{Ae}_6$  dimer formation imply the thermodynamic stability of the  $\text{BAe}_3$  clusters. Additionally, the binding energy per atom ( $E_b$ ) covers the 0.73–1.44 eV range and decreases in the order  $\text{BBe}_3$  (1.44 eV) >  $\text{BBa}_3$  (1.02 eV) >  $\text{BCa}_3$  (0.93 eV) >  $\text{BSr}_3$  (0.87 eV), implying the influence of composition and size on the cohesion of the  $\text{BAe}_3$  molecules.

To understand the regulation effect of the alkaline earth metal atoms on the redox properties of  $\text{BAe}_3$  clusters, the global minima and low-energy isomers of selected mixed  $\text{BAe}_3^{0/\pm}$  (Ae = Be, Mg, and Ca) clusters were optimized, which are shown in Fig. 1 and Fig. S1, respectively. In similarity to the non-mixed systems, mixed  $\text{BAe}_3$  ground states reveal that the B central atom binds with three Ae atoms forming a pyramidal-like structure. Linear and flat isomers are higher in energy by 0.34–5.79 eV, Fig. S1. As shown in Fig. 1, the detachment/attachment of one electron does not alter the whole structural framework, the pyramidal-like geometry, of  $\text{BAe}_3$ . The ionic mixed  $\text{BAe}_3^{\pm}$  (Ae = Be, Mg, and Ca) ground states feature the pyramidal-like geometry with the dihedral angle B–Ae<sub>1</sub>–Ae<sub>2</sub>–Ae<sub>3</sub>

Table 1 Free enthalpies ( $\Delta H_r^{298}$  in kcal mol<sup>-1</sup>), entropies [ $\Delta S_r^{298}$  in cal (mol K)<sup>-1</sup>], and Gibbs free energies ( $\Delta G_r^{298}$  in kcal mol<sup>-1</sup>) of the  $\text{BAe}_3 \rightarrow \text{BAe}_2 + \text{Ae}$  fragmentation reactions and the  $\text{BAe}_3 \rightarrow \frac{1}{2}\text{B}_2\text{Ae}_6$  dimer formation (at  $T = 298.15$  K,  $p = 1$  atm) obtained at the CCSD(T)/6-311+G(3df)+Def2TZVP level of theory for the  $\text{BAe}_3$  (Ae = Be, Mg, Ca, Sr, and Ba) ground states. For the higher energy fragmentation channels (i.e.,  $\text{BAe}_3 \rightarrow \text{BAe} + \text{Ae}_2$ ,  $\text{BAe}_3 \rightarrow \text{BAe} + 2\text{Ae}$ , and  $\text{BAe}_3 \rightarrow \text{B} + 3\text{Ae}$ ), see Section S4 in the SI)

Fragmentation path		$\Delta H_r^{298}$	$\Delta S_r^{298}$	$\Delta G_r^{298}$
$\text{BBe}_3 \rightarrow$	$\text{BBe}_2 + \text{Be}$	65.21	30.00	56.27
	$\frac{1}{2}\text{B}_2\text{Be}_6$	-2.32	-19.67	3.55
$\text{BBe}_2\text{Mg} \rightarrow$	$\text{BBe}_2 + \text{Mg}$	44.38	25.70	36.72
	$\text{BBeMg} + \text{Be}$	90.41	28.61	81.89
$\text{BBeMg}_2 \rightarrow$	$\text{BMg}_2 + \text{Be}$	52.13	26.20	44.32
	$\text{BBeMg} + \text{Mg}$	68.57	27.01	60.52
$\text{BBe}_2\text{Ca} \rightarrow$	$\text{BBe}_2 + \text{Ca}$	56.48	25.03	49.02
	$\text{BBeCa} + \text{Be}$	66.89	29.49	58.09
$\text{BMg}_3 \rightarrow$	$\text{BMg}_2 + \text{Mg}$	32.12	26.57	24.20
	$\frac{1}{2}\text{B}_2\text{Mg}_6$	-1.52	-17.93	3.82
$\text{BBeCaMg} \rightarrow$	$\text{BBeCa} + \text{Mg}$	42.46	27.92	34.14
	$\text{BBeMg} + \text{Ca}$	78.09	26.36	70.23
	$\text{BCaMg} + \text{Be}$	81.37	28.31	72.93
$\text{BCaMg}_2 \rightarrow$	$\text{BMg}_2 + \text{Ca}$	39.48	23.82	32.38
	$\text{BCaMg} + \text{Mg}$	64.48	47.69	50.27
$\text{BBeCa}_2 \rightarrow$	$\text{BBeCa} + \text{Ca}$	50.13	27.32	41.99
	$\text{BCa}_2 + \text{Be}$	84.65	25.55	77.04
$\text{BCa}_2\text{Mg} \rightarrow$	$\text{BCa}_2 + \text{Mg}$	60.70	23.91	53.57
	$\text{BCaMg} + \text{Ca}$	70.36	47.17	56.30
$\text{BCa}_3 \rightarrow$	$\text{BCa}_2 + \text{Ca}$	65.11	25.41	57.54
	$\frac{1}{2}\text{B}_2\text{Ca}_6$	-1.63	-19.38	4.14
$\text{BSr}_3 \rightarrow$	$\text{BSr}_2 + \text{Sr}$	38.03	28.94	29.40
	$\frac{1}{2}\text{B}_2\text{Sr}_6$	-2.27	-19.22	3.46
$\text{BBa}_3 \rightarrow$	$\text{BBa}_2 + \text{Ba}$	39.43	28.71	30.88
	$\frac{1}{2}\text{B}_2\text{Ba}_6$	-2.47	-19.22	3.26

**Table 2** Adiabatic ionization energy (AIE, in eV), vertical ionization energy (VIE, in eV), adiabatic electron affinity (AEA, in eV), and vertical electron affinity (VEA, in eV) values for the  $\text{BAe}_3$  (Ae = Be, Mg, Ca, Sr, and Ba) ground states estimated at the CCSD(T)/6-311+G(3df)+Def2QZVP//MP2(full)/6-311+G(3df)+Def2QZVP level. The lowest vibrational frequencies ( $V_1$ , in  $\text{cm}^{-1}$ ), HOMO–LUMO gaps (HL gap, in eV), and binding energies per atom ( $E_b$ , in eV) for the  $\text{BAe}_3^{0/\pm}$  (Ae = Be, Mg, Ca, Sr, and Ba) ground states

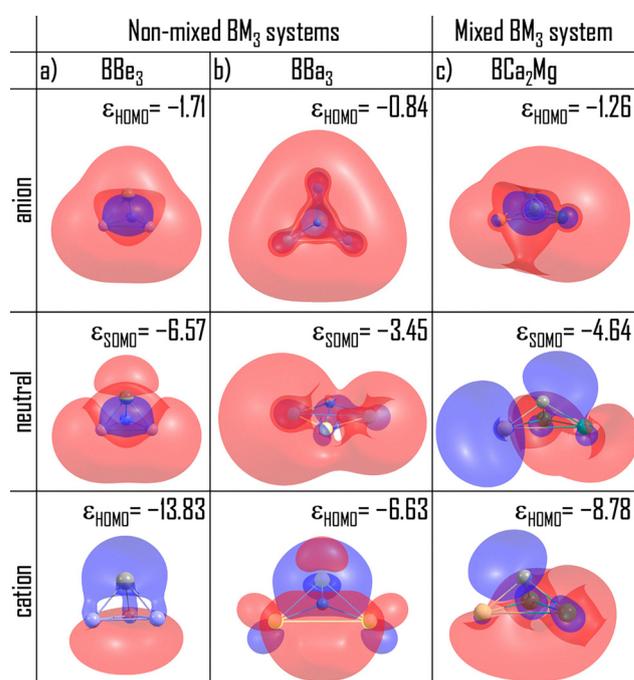
Cluster	Symmetry point group					Neutral			Cation			Anion		
		AIE	VIE	AEA	VEA	$V_1$	HL gap	$E_b$	$V_1$	HL gap	$E_b$	$V_1$	HL gap	$E_b$
$\text{BBe}_3$	$C_{3v}$	6.830	6.884	1.988	1.973	450	6.589	1.44	431	8.461	2.05	468	5.057	2.05
$\text{BBe}_2\text{Mg}$	$C_s$	6.147	6.191	1.708	1.698	290	5.664	1.19	290	7.802	1.53	292	4.200	1.73
$\text{BBMg}_2$	$C_s$	5.628	5.670	1.485	1.492	179	5.467	0.95	180	7.340	1.42	143	4.025	1.44
$\text{BBBe}_2\text{Ca}$	$C_s$	5.570	5.608	1.437	1.447	274	4.948	1.32	247	6.907	1.43	270	3.240	1.80
$\text{BMg}_3$	$C_{3v}$	5.221	5.267	1.294	1.341	158	5.360	0.73	175	7.035	1.31	142	3.973	1.18
$\text{BBBeCaMg}$	$C_1$	5.193	5.232	1.299	1.311	147	4.715	1.05	144	6.415	1.26	69	3.808	1.20
$\text{BCaMg}_2$	$C_s$	4.901	4.937	1.171	1.222	136	4.715	0.81	140	6.028	1.09	116	3.225	1.23
$\text{BBBeCa}_2$	$C_s$	4.835	4.861	1.168	1.189	118	4.570	1.14	108	5.775	1.43	103	3.052	1.55
$\text{BCa}_2\text{Mg}$	$C_s$	4.643	4.677	1.080	1.131	111	4.453	0.88	113	5.536	1.22	96	3.101	1.27
$\text{BCa}_3$	$C_{3v}$	4.462	4.485	0.990	1.053	122	4.348	0.93	120	5.176	1.32	102	3.092	1.29
$\text{BSr}_3$	$C_{3v}$	4.033	4.107	0.809	0.939	82	4.149	0.87	76	4.759	1.23	69	3.808	1.20
$\text{BBa}_3$	$C_{3v}$	3.818	3.765	0.435	0.939	58	3.504	1.02	57	3.964	1.29	56	3.282	1.24

in the 48–68° range. The B–Ae and Ae–Ae bonds are in the 1.773–2.524 Å and 2.055–3.954 Å range, respectively, in resemblance to typical B–Ae and Ae–Ae bonds.<sup>17,36</sup>

The difference between the vertical and adiabatic values of ionization energy and electron affinity offers valuable insight into the structural changes in a molecule upon electron loss and gain, respectively. Our CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df) results reveal that the difference between VIP and AIP does not exceed 0.074 eV for all  $\text{BAe}_3$  clusters, see Table 2. These small energy differences are accompanied by the pyramidal-like geometry of the cluster being preserved upon the  $\text{BAe}_3^+$  cation formation. Similarly, for most  $\text{BAe}_3$  species, the difference between VEA and AEA is small, being about 0.063 eV or less, implying minor geometry modification upon electron attachment. However, for  $\text{BSr}_3$  and  $\text{BBa}_3$ , notable differences between vertical and adiabatic electron affinities are observed (0.130 and 0.504 eV, respectively), which provoke substantial changes in the bond length of the corresponding anionic clusters, as illustrated in Fig. 2 and further analysed in the following section.

### 3.2. Double-Rydberg anions and their prospective in chemistry

The  $\text{BAe}_3$  clusters have adiabatic electron affinity in the 0.435–1.988 eV range (Table 2) and are, therefore, able to form stable anions. The HOMO analysis allows us to classify them as the double-Rydberg (DR) anions.<sup>50</sup> These DR anions consist of a closed-shell cation core (*i.e.*,  $\text{BAe}_3^+$  parent cation) plus two excess electrons described by Rydberg orbitals, Fig. 3. The B–Ae distances of  $\text{BMg}_3^-$  (2.178 Å),  $\text{BCa}_3^-$  (2.404 Å),  $\text{BSr}_3^-$  (2.519 Å), and  $\text{BBa}_3^-$  (2.593 Å) are shortened compared to those found for the corresponding non-charged species (by 0.084, 0.105, 0.108, and 0.127 Å, respectively) due to effective bonding of an additional electron, Fig. 1.<sup>17</sup> Moreover, the electron affinity of  $\text{BAe}_3$  molecules strongly depends on the molecular size. In general, a smaller alkaline earth metal (with a smaller atomic mass) leads to a larger AEA, and this observation agrees with the mathematical model for the electron affinity of superatom prediction.<sup>47</sup> According to this mathematical model,<sup>47</sup> there is a strong relationship between electron affinity and the nature of the orbitals



**Fig. 3** The highest occupied molecular orbitals (HOMOs) and singly occupied molecular orbitals (SOMOs) of the ground state structures of representative (a) and (b) non-mixed and (c) mixed  $\text{BAe}_3^\pm$  ions and their neutral  $\text{BAe}_3$  parents, respectively. The HOMOs and SOMOs are plotted with a fraction of electron density ( $F_e$ ) equal to 0.8 and their eigenvalues ( $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{SOMO}}$ , respectively) are in eV. Contour values used in the plots were obtained with the OpenCubeMan rev.0.01 for  $F_e = 0.8$ .<sup>45</sup>

involved in the electron addition. Explicitly, the principal quantum number of the last electronic shell defines the size of the orbital and the energy of an additional electron. As the principal quantum number decreases, the orbital becomes smaller, and the electron density is closer to the nucleus. Also, as the principal quantum number of the last electronic shell decreases, the extra electron has lower potential energy and is, therefore, more tightly bound to the nucleus. Hence, introducing alkaline earth metals with a smaller principal quantum number of the last electronic shell results in an increase in electron affinity.



Based on the *ab initio* calculations, we demonstrated the ability of the  $\text{MAe}_3^+$  closed-shell molecular cations to attach two electrons to their Rydberg orbitals to form double Rydberg anions. This class of anions was first experimentally confirmed in 1987 by Bowen and Eaton, who measured the electron binding energy of the  $\text{NH}_4^-$  anion to be 0.5 eV using a photodetachment experiment.<sup>51</sup> Later that year, Ortiz employed electronic structure calculations to predict that a tetrahedral closed-shell  $\text{NH}_4^+$  cation surrounded by two electrons in a Rydberg-like orbital would have an electron binding energy of 0.42 eV.<sup>52</sup> Since then, numerous theoretical studies have been made to estimate the electron binding of various double Rydberg anions, including  $\text{H}_3\text{C-NH}_3^-$ ,  $\text{NH}_3\text{NH}_2^-$ ,  $\text{NH}_3\text{OH}^-$ ,<sup>53</sup> and  $\text{N}_4\text{Mg}_6\text{M}^-$  ( $\text{M} = \text{Li}, \text{Na}, \text{and K}$ ).<sup>17</sup> We believe that the  $\text{BAe}_3^-$  double Rydberg anions designed and investigated here can exist at low temperatures in the gas phase (as an isolated species in the absence of any perturbations).

### 3.3. Electron localization function (ELF)

The ELF is a measure of electron localization and its usefulness for a superatomic system study is described elsewhere.<sup>17,21,22</sup> The normalized  $\text{ELF} = 1.0$  represents perfect localization (e.g., covalent bond and inner shell electrons), while the  $\text{ELF} = 0.5$  corresponds to electron-gas-like probability. The topological analysis of the ELF leads to a partition into several “basins” that can be mapped to chemical concepts: core electrons, bonds, and lone pairs.<sup>21</sup> Fig. 4 shows valence basins located between the alkaline earth metal (Ae–Ae) atoms as well as boron and alkaline earth metal (B–Ae) atoms, indicating that the covalent-like bonds are formed between Ae–Ae and B–Ae atoms,

respectively. A strong electron density delocalization ensures an enhanced electronic stability of the  $\text{BAe}_3$  systems. As shown in Fig. 4, the electron delocalization ( $\text{ELF} = 0.5$ , coloured in green) reduces with the change of the ionization from an anion through neutral to a cation. Upon electron detachment, the electron delocalization reduces and valence electrons become more localized between atoms in the form of directional chemical bonds.

### 3.4. Adiabatic ionization energies of $\text{BAe}_3$ clusters

Furthermore, to investigate whether the alkaline earth metal substitution process can enhance the capability of the clusters in detaching electrons, we calculated the AIE of clusters (Table 2). In Table 2, compounds are sorted by ascending molecular mass. In general, introducing larger alkali earth metals decreases the ionization energy, representing the electron-donor capability, of the  $\text{BAe}_3$  clusters. Strikingly,  $\text{BBa}_3$  was estimated to possess the lowest AIE value here (3.818 eV), exhibiting the superalkali characteristic, which is smaller than the lowest IE among alkali elements (Cs, 3.89 eV). We observed a monotonic AIE decrease with an increase in molecular size for all  $\text{BAe}_3$  species.

The AIE depends on atomic mass. Different alkaline earth metal substituents affect the ionization energy of the  $\text{BAe}_3$  system. We observed the most striking difference while comparing the  $\text{BBa}_3/\text{BSr}_3/\text{BCa}_3/\text{BMg}_3/\text{BBe}_3$  set, as the replacement of three Ba atoms with three Sr, Ca, Mg or Be atoms leads to the ionization energy increase from 3.818 eV ( $\text{BBa}_3$ ) to 4.033 eV ( $\text{BSr}_3$ ), 4.462 eV ( $\text{BCa}_3$ ), 5.221 eV ( $\text{BMg}_3$ ), and 6.830 eV ( $\text{BBe}_3$ ). The same pattern was found for the  $\text{BCa}_3$  (4.462 eV)/ $\text{BCa}_2\text{Mg}$  (4.643)/ $\text{BBeCa}_2$  (4.835 eV) and  $\text{BCa}_3$  (4.462 eV)/ $\text{BCaMg}_2$  (4.901)/ $\text{BBe}_2\text{Ca}$  (5.570 eV) series, where mixed substituents were introduced by replacing one or two Ca atoms with either Mg or Be atoms. This significant increase in the AIE value caused by atomic composition modification shows that the larger the atomic mass of the alkaline earth metal atom, the smaller the AIE of the resulting  $\text{BAe}_3$  cluster. This implies that the electronic stability of the  $\text{BAe}_3$  clusters (Ae = Be, Mg, Ca, Sr, and Ba) can be predicted from the atomic mass of the atoms comprising the superalkali-like systems. The lowest ionization energy values are expected for species containing electropositive substituents characterized by a large atomic mass. The above observation indicates that replacing a substituent in the superalkali-like system with a larger atom is highly favorable because it reduces electronic stability and enhances the reducing ability. This finding once again proves that suitable electropositive metals that the central atom is decorated with can regulate the electronic properties of the molecular cluster forming a superalkali.<sup>3,17,21,54</sup>

### 3.5. Superatomic electronic structure

The singlet spin state  $\text{BAe}_3^+$  cations (Fig. 2) have a superatomic nature and follow the jellium model. According to the jellium model, the valence electrons are in quantized superatomic orbitals ( $1\text{S}^2|1\text{P}^6|1\text{D}^{10}|2\text{S}^2, 1\text{F}^{14}|2\text{P}^6, 1\text{G}^{18}|\dots$ ) distributed over the cluster. The superatomic clusters enhance their stability when the electronic shells are closed.<sup>55</sup> The  $\text{BAe}_3$  neutral system has nine valence electrons ( $3 + 3 \times 2$ ), thus one additional

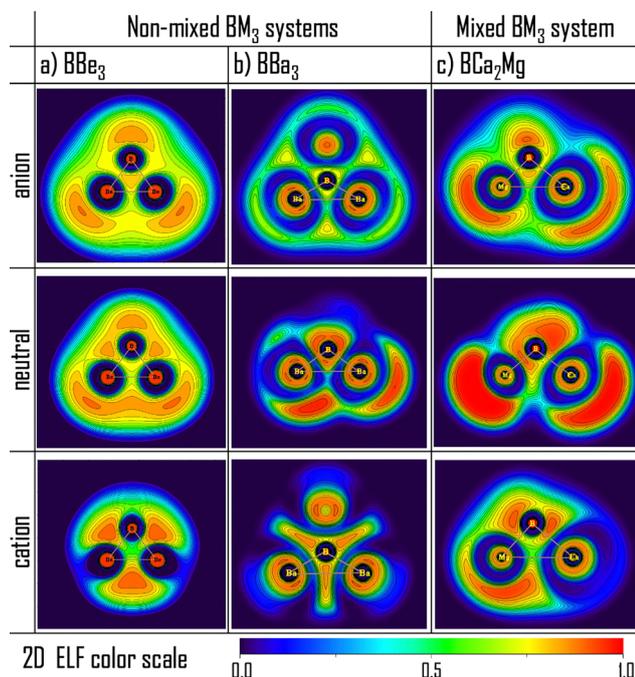


Fig. 4 Cut-plane electron localization function (ELF) plots of representative (a) and (b) non-mixed and (c) mixed anionic (top), neutral (middle), and cationic (bottom)  $\text{BAe}_3$  clusters in the B–Ae<sub>1</sub>–Ae<sub>2</sub> plane. The ELF plots were obtained with the Multiwfn v.3.8. software.<sup>42,43</sup>



electron than needed for the octet shell closure, in analogy to alkali atoms. The  $\text{BAe}_3$  cluster can be seen as a doublet spin state open-shell superatomic structure (Fig. 2) with nine delocalized valence electrons. The thermodynamic stability accorded with the closure of the electronic shell meaning that  $\text{BAe}_3^+$  cations have a  $1S^2|1P^6$  electronic structure and their highest occupied molecular orbitals (HOMOs) have p-character, see Fig. 3. The closed-shell electron configuration of valence electrons determines the enhanced stability of the  $\text{BAe}_3^+$  superatomic compounds.

The  $\text{BAe}_3^+$  cations have large electronic stabilities. Their HOMO eigenvalues span the  $-13.82$  eV ( $\text{BBe}_3^+$ , Fig. 3a) to  $-6.63$  eV ( $\text{BBa}_3^+$ , Fig. 3b) range. The singly occupied molecular orbitals (SOMOs) of  $\text{BAe}_3$  neutral parents are highly delocalized over the whole cluster, which ensures the reduction of repulsion interaction between electrons. Also, the highly diffused SOMO emphasizes that the outermost electron is loosely bound to the nuclei, giving rise to the low ionization energy. The SOMO character determines the reducing potential of  $\text{BAe}_3$  clusters. We distinguish the difference in the SOMO nature of non-mixed and mixed systems. In the case of mixed clusters, the SOMO reveals the antibonding character with respect to the B–Mg (Fig. 3c) and bonding B–Be (Fig. S6d in the SI) interactions. In turn, the non-mixed cations have a bonding nature of all B–Ae interactions (Fig. 3a and b). The described alteration in the SOMO nature leads to symmetry breaking in mixed neutral clusters and subsequently decreases the electron stability and enhances the reducing potential of the resulting systems.

In the neutral superatom framework, it will be the delocalized valence electrons that determine the diamagnetic behaviour. Although a single unpaired electron would be expected to align parallel to the external applied field, the global ring current around the  $\text{BAe}_3$  clusters results in substantial antiparallel alignment.<sup>56</sup> All  $\text{BAe}_3$  species contribute to the diamagnetic susceptibility (with values ranging from  $-3.18 \times 10^{-6}$  to  $-3.73 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ ) with small paramagnetic contributions (ranking from  $1.78 \times 10^{-5}$  to  $2.81 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ , Fig. S9 of the SI). The total magnetic susceptibility, derived as the sum of diamagnetic and paramagnetic contributions, remains weakly negative (from  $-4.51 \times 10^{-6}$  to  $-1.95 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ ), indicating an overall weak diamagnetism of the  $\text{BAe}_3$  clusters. The observed diamagnetism is distinctive for superatoms with delocalized electrons.<sup>56</sup>

### 3.6. Natural bond orbital (NBO) analysis

As shown in Fig. 5a, the molecular size of the alkaline earth metals determines the ionization energy of the resulting clusters, which changes from the nonalkali ( $\text{BBe}_3$ , AIE = 6.830 eV) to the alkali ( $\text{BBa}_3$ , AIE = 3.818 eV) nature with the increment of alkaline earth metals' size. The interaction between boron and alkaline earth metal atoms has an electrostatic character. To check the charge distribution in the designed clusters, we performed the charge analysis using the natural bond orbital (NBO) approach. As can be seen from Fig. 5, the B atom gains electron density from Ae atoms, verifying the electron-withdrawing characteristic of the boron atom. The electrons of the Ae atoms enter either an antibonding (mixed clusters) or a bonding (mixed and non-mixed clusters) molecular orbital of the boron atom, and the energy of

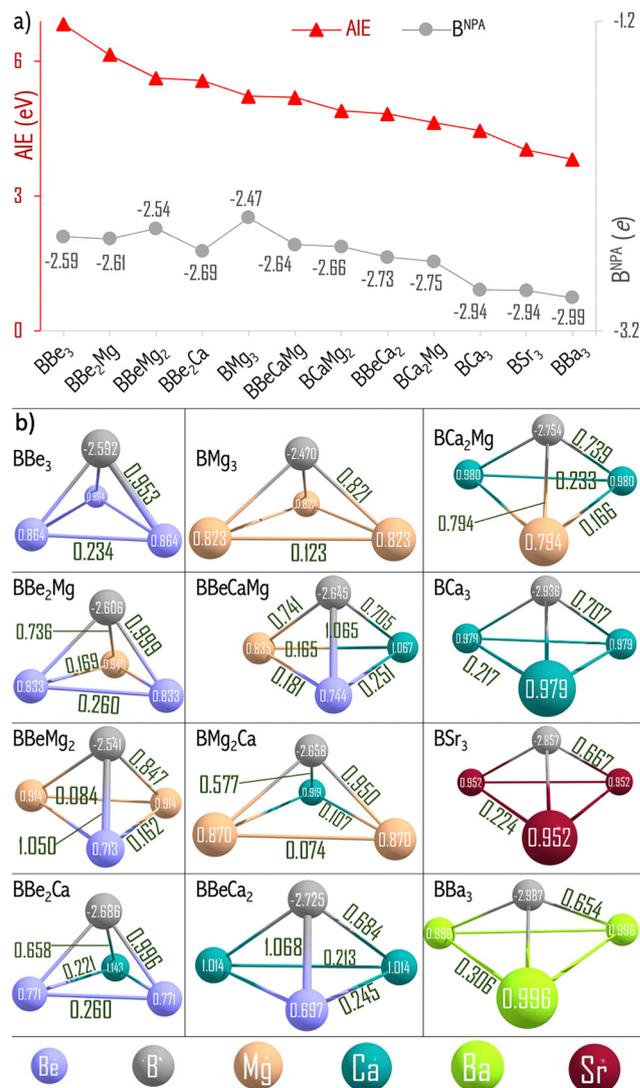


Fig. 5 (a) The adiabatic ionization energy (AIE, in eV) and natural charge on the boron atom by NBO analysis ( $B^{\text{NPA}}$ , in e) of the MP2(full)/6-311+G(3df)  $\text{BAe}_3$  ground state structures. Clusters have been sorted by ascending molecular mass. (b) Natural atomic charges (in e) and Wiberg bond indexes (in green) by natural population analysis (NPA).

their bond in the  $\text{BAe}_3$  molecule will be respectively lower or higher than in the isolated Ae atom. Such a continuous charge transfer (Fig. 5) between B and Ae atoms could enhance the electrostatic interaction between these boron and alkaline earth metal atoms, which produces  $\text{BAe}_3$  clusters. The strength of the bond between B and Ae atoms in the  $\text{BAe}_3$  clusters can be further evaluated by the Wiberg bond index (WBI, Fig. 5b) analysis. The relative B–Ae bond strength hierarchy given by WBI values in the non-mixed  $\text{BAe}_3$  species is in the order B–Be (0.953) > B–Mg (0.821) > B–Ca (0.707) > B–Sr (0.667) > B–Ba (0.654), which implies that the B–Ae bond strength decreases as the atomic size of the alkaline earth metal increases. The stronger B–Be bond likely results from stronger covalent interactions, where boron's smaller atomic size allows for better overlap with the 2s orbital of beryllium, creating a stronger bond. Descending the group, the



larger ionic radii of Mg, Ca, Sr, and Ba result in poorer orbital overlap with boron, leading to a decrease in bond order.

The neutral  $\text{BAe}_3$  clusters are open-shell systems with one unpaired electron (their ground electronic states are doublets, Fig. 2). These radical compounds have 34–89% spin density on the boron atom (Fig. S8 of the SI), due to its lower electronegativity in comparison with electropositive alkali earth metal substituents. The natural spin density localized on the boron atom in the non-mixed  $\text{BAe}_3$  species gradually increases in the order  $0.492 (\text{BBe}_3) < 0.825 (\text{BMg}_3) < 0.872 (\text{BCa}_3) > 0.893 (\text{BSr}_3) > 0.894 (\text{BBa}_3)$ , which implies that the spin density on the B atom increases as the atomic size of the alkaline earth metal increases. Although the spin is largely localized on the B central atom, a significant part of the spin density is delocalized onto the Ae ligands. This is supported by natural spin density values on the Be (0.127–0.183), Mg (0.022–0.070), Ca (0.043–0.071), Sr (0.036), and Ba (0.035) atoms.

The linear-like trend in how the alkaline earth metal substitution modulates the AIE of  $\text{BAe}_3$  clusters may be linked to the change in the frontier molecular orbital (MO) energies. It is well-known that the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels determine a species' ability to accept and donate electrons, respectively. Correspondingly, as shown in Fig. 6, the variation trend of the singly occupied molecular orbital (SOMO) levels of the  $\text{BAe}_3$  clusters is in excellent agreement with that of the adiabatic ionization energy values. In addition, the HL gap of the cluster can be considered as one signature of enhanced stability and reduced reactivity. As shown in Fig. 6, the HL gap reduces as the molecular mass increases. Such a result of the HL gap is also consistent with the calculated AIE values.

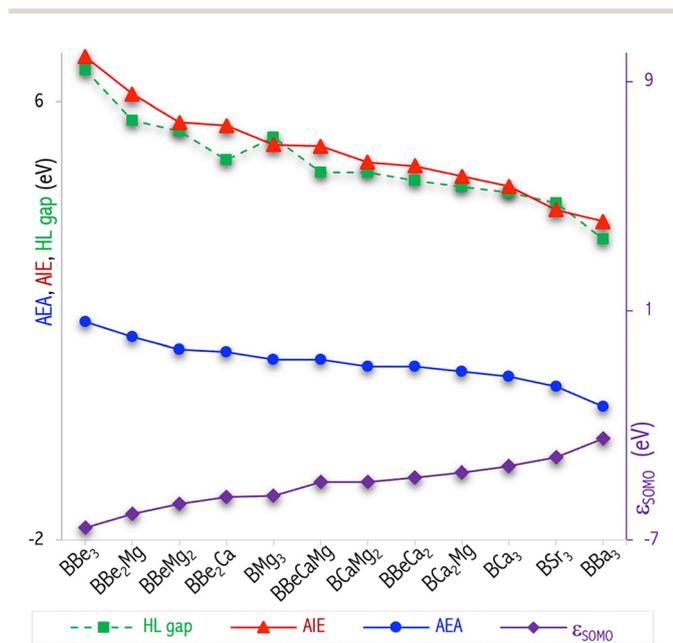


Fig. 6 The adiabatic electron affinity (AEA), adiabatic ionization energy (AIE), HOMO–LUMO gap (HL gap), and eigenvalue of singly occupied molecular orbital ( $\epsilon_{\text{SOMO}}$ ) of neutral  $\text{BAe}_3$  clusters. Corresponding estimated data are listed in Table S3.

Consequently, the higher stability of the  $\text{BAe}_3$  clusters results in their lower reducibility. This finding proves that suitable electropositive metals with which the central atom is decorated can regulate the electronic properties of molecular clusters forming a superalkali.

### 3.7. Empirical models for adiabatic ionization energy

To suggest an effective approach that could be used to predict the electron-donating ability of molecular clusters, we decided to develop mathematical models for ionization energy prediction. The developed models are described and discussed in Section S9 of the SI, while the most significant equations are provided in Fig. 7. Careful inspection of calculated AIE values (Fig. 7a) reveals that an accurate quadratic polynomial function can be fitted with a correlation coefficient value of 0.99 ( $R^2$ ), which is  $\text{AIE} = 23.56 - 15.16 \cdot x + 2.91 \cdot x^2$ , where  $x$  represents a decimal logarithm of molecular mass ( $\log_{10} M$ ). Having such a relationship between the AIE and atomic properties, one can realize the precise regulation of the ionization energy of  $\text{BAe}_3$  because the main feature of the superatomic systems is their atomic-precise tunability. For example, one can acquire the 6.83 eV AIE value of  $\text{BAe}_3$  by synthesising a non-mixed beryllium-based molecular cluster. The electronic stability can be modulated *via* alkaline earth metal substitution. Replacing only one Be substituent in the  $\text{BBe}_3$  system with larger Mg or Ca atoms is highly favorable because it enhances the reducing ability by 0.68 eV ( $\text{BBe}_2\text{Mg}$ ) and 1.26 eV ( $\text{BBe}_2\text{Ca}$ ), respectively. Such precise tunability of the electronic properties of the cluster upon structural modification represents a significant advantage in the superalkali construction strategy.

Similarly, well-fitting functions can be obtained by linking the cluster's ionization energy and a sum of ionization energies of constituent atoms as well as the Pauling electronegativity of atoms. The estimated quadratic  $\text{AIE} = 6.85 - 0.36x + 0.01x^2$  (where  $x$  represents the sum of atomic ionization energies, Fig. 7b) and linear  $\text{AIE} = -1.80 + 1.19x$  (where  $x$  represents the sum of electronegativity, Fig. 7c) functions reveal  $R^2$  equal to 0.98 and 0.99, respectively. Also, the sum of atomic radii allows us to predict the ionization energy of the  $\text{BAe}_3$  cluster from the polynomial  $\text{AIE} = 22.02 - 3.53 \cdot x + 0.17 \cdot x^2$  ( $R^2 = 0.93$ , Fig. 7d) function. These findings demonstrate that the proposed substitution-based strategy for designing superalkali-like clusters works for the  $\text{BAe}_3$  systems investigated here and can be applied to different superatomic systems. Thus, the proposed substituent modification-based strategy provides a potential methodology for constructing superalkalis for the chemical synthesis of atomically precise clusters, that is, applying suitable alkaline earth metals to synthesize stable molecular clusters having desirable ionization energy.

### 3.8. QSPR modeling

To further investigate the ability to predict the ionization energy of a superalkali cluster from its atomic features, we performed the quantitative structure–property relationship (QSPR) approach. The QSPR method mathematically links physicochemical properties with the structure of a molecule. The usefulness of this method has been confirmed for superatomic compounds (such as superhalogens).<sup>47,57,58</sup> The methodology applied is described



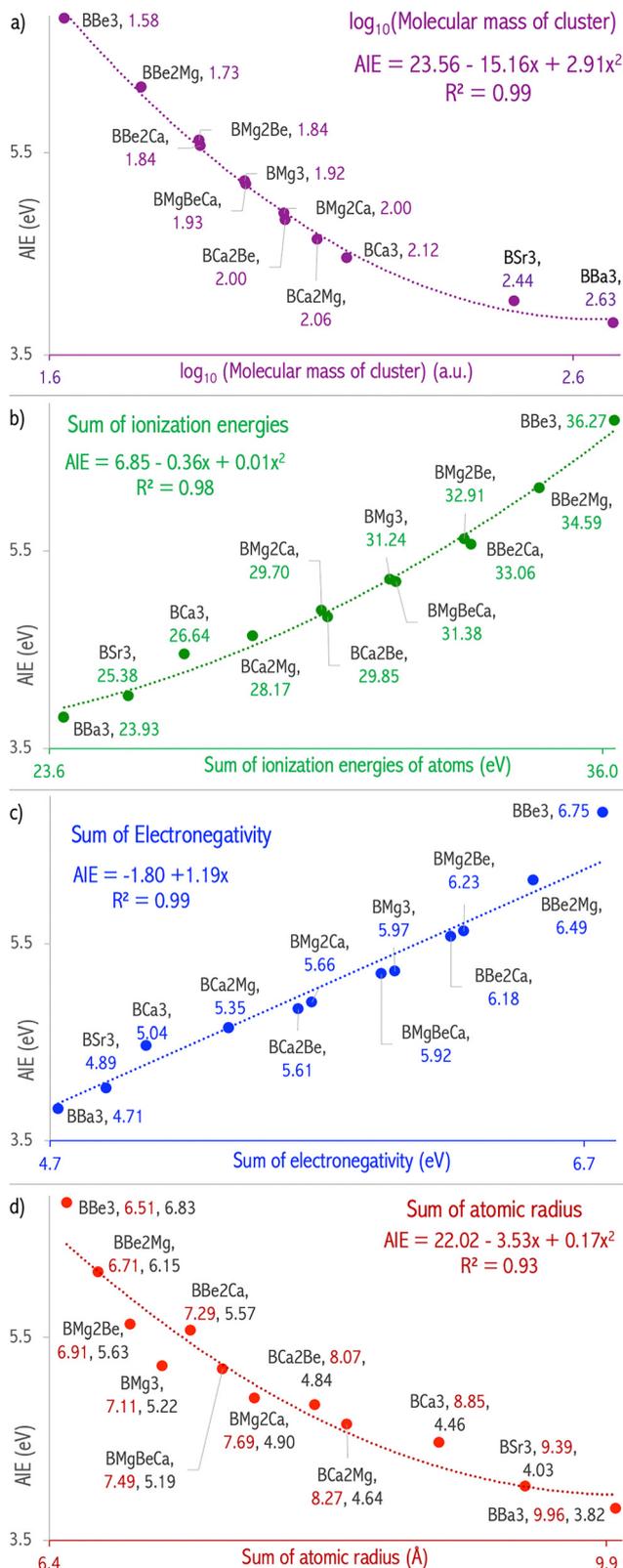


Fig. 7 Empirical models to predict adiabatic ionization energy of boron-based clusters from (a) decimal logarithm of molecular mass of a cluster ( $\log_{10}M$ ), (b) sum of ionization energies of constituent atoms, (c) sum of Pauling electronegativity of constituent atoms, and (d) the sum of atomic radius.

elsewhere<sup>47</sup> and involved the following steps: (i) splitting the compounds into training and validation sets, (ii) calibrating a QSPR model, and (iii) internally and externally validating the model with the use of test and validation sets, respectively. In Table 3, the  $\text{BAe}_3$  compounds were sorted in descending order of the AIE values, and then every second molecule was included in the test set (V), while the remaining compounds formed the training set (T). The above splitting algorithm leads to a uniform distribution of training and validation sets within the entire range of the AIE values. As a result, the  $\text{BAe}_3$  clusters were separated into two independent subsets: a training set of 7 compounds to build a QSPR model and a test set of 5 compounds to evaluate the prediction ability of the developed model. The most significant QSPR model (eqn (11), where the descriptor represents the square of a sum of ionization energies of constituent atoms) exhibits determination coefficient ( $R^2$ ), cross-validation determination coefficient ( $Q_{\text{CV}}^2$ ), and external validation coefficient ( $Q_{\text{EXT}}^2$ ) values close to 1, while the corresponding root mean square error values ( $\text{RMSE}_{\text{C}}$ ,  $\text{RMSE}_{\text{CV}}$ , and  $\text{RMSE}_{\text{EXT}}$ , for their formulas see Section S10 in the SI), are both low and similar. Also, the visual correlation between the observed and predicted AIEs for the training (blue circles) and validation (red rectangles) sets illustrates the model's predictive capability (Fig. 8a).

$$\text{AIE} = 1.468(\pm 0.167) + 0.004(\pm 1.801 \times 10^{-4}) \times \left( \sum_{i=1}^{n_{\text{At}}} \text{IE}_i \right)^2 \quad (11)$$

$$R^2 = 0.990 \quad Q_{\text{CV}}^2 = 0.965 \quad Q_{\text{EXT}}^2 = 0.917$$

$$\text{RMSE}_{\text{C}} = 0.096 \quad \text{RMSE}_{\text{CV}} = 0.176 \quad \text{RMSE}_{\text{EXT}} = 0.168$$

In the next step, we used the leverage approach<sup>59</sup> to verify the chemical applicability domain of the developed model. The plot of the standardized residuals *versus* the leverage values ( $h_i$ , the Williams plot, Fig. 8b) confirmed that all  $\text{BAe}_3$  molecules from the calibration and validation sets were established inside a squared area within  $\pm 3$  standard deviation units and the leverage threshold ( $h^* = 0.86$ , green dashed line in Fig. 8b). The warning leverage,  $h^*$ , is fixed at  $3(m+1)/n$ , where  $m$  is the number of descriptors involved in a QSPR equation and  $n$  is the number of compounds in the training set. In the Williams plot (Fig. 8b), neither training nor validation compounds are identified as X or Y-outliers, implying that their predictions are highly reliable. Thus, the QSPR model can be successfully applied to predict the reducibility of  $\text{BAe}_3$  superalkali clusters and other untested superalkalis under the condition that the calculated  $h_i$  value for such a chemical structure is lower than the critical one ( $h^* = 0.86$ ).

The interpretation of the physical meaning of the descriptor used in the developed QSPR model suggests that the ionization energy of the  $\text{BAe}_3$  clusters ( $\text{Ae} = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{and Ba}$ ) can be predicted from the sum of ionization energies of the atoms comprising the superalkali systems. The developed QSPR model implies that introducing more electron-donating substituents



**Table 3** Adiabatic ionization energies estimated at the CCSD(T)/6-311++G(3df,3pd)+Def2QZVP level ( $AIE^{OBS}$ , in eV) and predicted by the QSPR model ( $AIE^{PRED}$ , in eV) for the  $BAe_3$  (Ae = Be, Mg, Ca, Sr, and Ba) ground states. The differences between  $AIE^{OBS}$  and  $AIE^{PRED}$  are given by residual values (in eV).

The sum of first ionization energies of the atoms comprising the  $BAe_3$  cluster ( $\sum_{i=1}^{nAt} IE_i$ , in eV) and its square value ( $(\sum_{i=1}^{nAt} IE_i)^2$  in eqn (11)). The compounds were split into a training set (T, later used for developing the QSPR model) and an external validation set (V, later used for evaluating the predictive ability of the model)

Compound	$AIE^{OBS}$	$AIE^{PRED}$	Residual	Sum of ionization energies ( $\sum_{i=1}^{nAt} IE_i$ )	$(\sum_{i=1}^{nAt} IE_i)^2$	Dataset splitting
BBe <sub>3</sub>	6.830	6.673	0.157	36.27	1315.295	T
BBe <sub>2</sub> Mg	6.147	6.202	-0.055	34.59	1196.468	V
BBeMg <sub>2</sub>	5.628	5.754	-0.126	32.91	1083.266	T
BBe <sub>2</sub> Ca	5.570	5.792	-0.222	33.06	1092.765	V
BMg <sub>3</sub>	5.221	5.329	-0.108	31.24	975.688	T
BBeCaMg	5.193	5.364	-0.171	31.38	984.704	V
BCaMg <sub>2</sub>	4.901	4.959	-0.058	29.70	882.268	T
BBeCa <sub>2</sub>	4.835	4.993	-0.158	29.85	890.843	V
BCa <sub>2</sub> Mg	4.643	4.608	0.035	28.17	793.549	T
BCa <sub>3</sub>	4.462	4.275	0.187	26.64	709.530	V
BSr <sub>3</sub>	4.033	4.017	0.016	25.38	644.297	T
BBa <sub>3</sub>	3.818	3.734	0.084	23.93	572.836	T

decreases the ionization energy, representing the electron-donor capability, of the  $BAe_3$  clusters. Strikingly,  $BBa_3$  was estimated to possess the lowest AIE value here (3.82 eV), which is smaller than the lowest IE among alkali elements [3.89 eV (cesium atom)]. The developed mathematical model demonstrates that the electronic properties of molecular clusters forming the superalkali can be tuned upon an atom substitution within it.

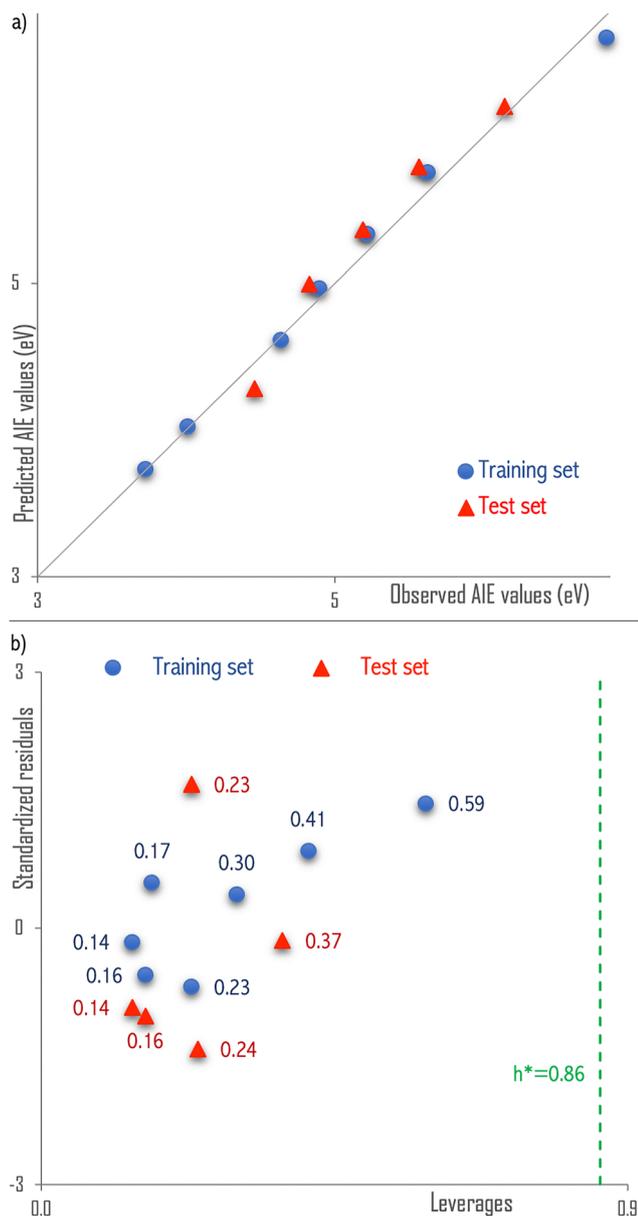
To sum up, based on only one theoretical molecular descriptor, calculated exclusively from the molecular structures, we developed a QSPR model to estimate adiabatic ionization energies of the  $BAe_3$  (Ae = Be, Mg, Ca, Sr, and Ba) superalkalis. The descriptor used, as a constitutional descriptor, does not depend on the conformation of a molecule or atom connectivity and only uses the atom information of the molecule for the calculation. The developed QSPR model, therefore, allows for the prediction of the ionization energy of a superalkali cluster based on the chemical composition of a molecule. The advantage of this approach lies in the fact that it requires only the knowledge of the chemical composition and does not require experimental quantities or quantum-mechanical computations. Hence, the developed QSPR model could provide reliable AIE values of superalkalis in the absence of theoretical characterization (e.g., due to insufficient computer resources). Moreover, the QSPR model identifies the ionization energy of the atoms contributing the superalkalis as the most influential atomic property in determining the reducing capabilities of these superalkali clusters. We believe that the QSPR model and its interpretation, which we provided above, might be useful for theoretical and experimental chemists, especially those who design new materials with strong electron-donor features.

### 3.9. $BAe_3$ clusters as reducing agents for carbon dioxide activation

The  $BAe_3$  clusters have low ionization energy and can be used as electron donors to reduce counterpart systems with low

electron affinity. Hence, in the next step, we investigated the reducing effect of the  $BAe_3$  clusters on the  $CO_2$  molecule. Various binding sites for the  $CO_2$  molecule on  $BAe_3$  were extensively considered to determine the global minima of these complexes (see the SI for the low-energy isomers of  $BAe_3/CO_2$ ). As shown in Fig. S10, S11 and Fig. 10, the  $BAe_3$  interaction process leads to the deformation of the neutral  $CO_2$  molecule, which changes from a linear geometry to a bent structure. The O–C–O valence angle reduces from linear to 110–133° upon the interaction with  $BAe_3$ , exhibiting its bent form. This implies that the interaction between  $BAe_3$  and  $CO_2$  is relatively strong. Additionally, in the  $BAe_3/CO_2$  species (Fig. S10 and S11), the  $CO_2$  subunit exhibits the bridging mode, where either the oxygen atom binds with alkaline earth metal or the carbon atom binds with Ae or B atoms, forming a covalent-like bond. Next, the binding energies (BEs, eqn (8)) of the  $CO_2$  molecule onto the  $BAe_3$  neutral clusters were explored to elucidate the interaction strength between the  $CO_2$  molecule and a  $BAe_3$  cluster (Fig. 9), which can also be used to estimate the stability of these interacting species. Since an effective catalyst must bind intermediates strongly enough to activate them, yet weakly enough to allow product release, the magnesium-based  $BAe_3$  clusters emerge as promising candidates for  $CO_2$  activation (the interaction strength is below 1 eV). The NBO charge transfer from the Mg-based  $BAe_3$  clusters to the  $CO_2$  molecule ( $Q_{CO_2}^{NBO}$ ) is from 0.88e ( $BBe_2Mg/CO_2$ ) to 0.95e ( $BCa_2Mg/CO_2$ ), which exceeds those gained by the  $CO_2$  molecule from  $Li_3F_2$  (0.63e),<sup>60</sup>  $C_5NH_6$  (0.77e),<sup>61</sup>  $N_4Mg_6Li$  (0.80e),<sup>17</sup>  $N_4Mg_6Na$  (0.80e),<sup>17</sup>  $N_4Mg_6K$  (0.81e),<sup>17</sup>  $NLi_4$  (0.85e),<sup>62</sup>  $OLi_3$  (0.88e),<sup>62</sup>  $B_3C_3H_{12}$  (0.89e),<sup>61</sup>  $Mn(B_3N_3H_6)_2$  (0.90e),<sup>61</sup> and  $FLi_2$  (0.90e).<sup>62</sup> The  $Q_{CO_2}^{NBO}$  of the remaining  $BAe_3/CO_2$  systems exceeds 1.25e, comparable to that observed in the  $Al_3/CO_2$  complex (1.26e).<sup>61</sup> As shown in Fig. 9, the estimated BE values approach -3.21 eV, which implies a larger intermolecular interaction than those of the  $N_4Mg_6M/CO_2$  (M = Li, Na, and K) species (BE values from -1.64 to -1.57 eV as obtained at the CCSD(T)/6-311+(3df) level<sup>17</sup>). Such large BE values probably stem from the





**Fig. 8** (a) The plot of observed vs. predicted AIEs (in eV). (b) The Williams plot of the developed QSPR model. The Williams plot compares the leverage values ( $h_i$ , eqn (S1)) and standardized cross-validated residual values ( $AIE_{obs} - AIE_{pred,cv}$ ). The green dashed vertical line corresponds to the leverage threshold ( $h^* = 0.86$ ). The leverage threshold is defined as  $h^* = 3(m + 1)/n$ , where  $m$  is the number of descriptors involved in a QSPR equation and  $n$  is the number of compounds in the training set.

C–B, C–Ae, and O–Ae bridging modes, the charge transfer from the superalkali to carbon dioxide, and indicate the high stability of these  $BAe_3/CO_2$  systems as well.

### 3.10. The role of the singly occupied molecular orbital (SOMO) in stabilizing the anionic form of carbon dioxide

A superalkali, acting as an electron donor, facilitates the reduction of carbon dioxide. The singly occupied molecular orbital (SOMO) of representative  $BMg_3/CO_2$  species is mainly

contributed by atomic orbitals of the carbon dioxide counterpart, rather than the  $BMg_3$  cluster, as would be expected in a charge transfer  $[superalkali]^+[CO_2]^-$  compound.<sup>17</sup> This observation implies a reduced form of carbon dioxide in the superalkali/ $CO_2$  chemical system. The visualized HOMO and SOMO of  $CO_2$  and  $CO_2^-$ , respectively, shown in Fig. 10 illustrate how the molecular structure alters upon the attachment of an excess electron. The neutral carbon dioxide molecule adopts a linear geometry, with its p-type HOMO and HOMO – 1 orbitals consisting of lone pair electrons of oxygen atoms (Fig. 10e). Upon gaining an additional electron, the point group of  $CO_2$  changes from  $D_{\infty h}$  to  $C_{2v}$ . The excess electron occupies the  $\sigma^*$  antibonding orbital of carbon dioxide, and the hybridization of the carbon atom shifts from sp to  $sp^2$ -like as it accepts the electron, transforming into the  $CO_2^-$  anion. This change in hybridization triggers a bending of the carbon dioxide structure resulting in a  $CO_2^-$  anion (Fig. 10d).<sup>61</sup> In the  $BMg_3/CO_2$  compound (Fig. 10c), the SOMO resembles the SOMO antibonding orbital of the  $CO_2^-$  anion (Fig. 10d). The HOMO – 1, HOMO – 2, and HOMO – 3 orbitals resemble the three highest occupied molecular p-type orbitals of the  $BMg_3^+$  cation. Since  $CO_2$  adopts a bent structure upon electron transfer or due to its interaction with the electrons of the metal atom (Fig. 10c),<sup>17,61</sup> the electron is transferred from a Rydberg-like orbital of open-shell  $BMg_3$  cluster (Fig. 10a) to the  $\sigma^*$  antibonding LUMO of carbon dioxide (Fig. 10e) to form the  $[BMg_3]^+[CO_2]^-$  ionic compound.

As demonstrated above, the carbon dioxide moiety undergoes significant geometry relaxation upon interaction with the  $BAe_3$  cluster to form the resulting  $BAe_3/CO_2$  compound. Specifically, the structural changes in  $CO_2$  upon interaction with the  $BAe_3$  superalkali molecule convert its linear geometry toward the bent structure of  $CO_2^-$  anion. Although the final anionic structure of carbon dioxide is not entirely achieved in the superalkali/ $CO_2$  product, this observation indicates the electron density donation, which takes place when a superalkali combines with a  $CO_2$  molecule.

### 3.11. The mechanism of the $CO_2$ activation

The activation of the carbon dioxide molecule upon its interaction with a superalkali can be explained by choosing one representative system and determining the eventual kinetic (*i.e.*, activation) barrier that must be overcome to create the resulting  $[superalkali]^+[CO_2]^-$  ionic compound. We decided to investigate the process by assessing the energy change that accompanies the reaction of substrates (superalkali and  $CO_2$ ), leading to the creation of the  $CO_2^-$  anion for an arbitrarily chosen  $BMg_3/CO_2$  system. While analyzing the energy profile for the  $BMg_3 + CO_2 \rightarrow [BMg_3]^+[CO_2]^-$  process, the excess electron must be assigned to  $BMg_3$  rather than to  $CO_2$  (for the separated  $BMg_3$  and  $CO_2$  systems) due to the considerably larger electron affinity of the  $BMg_3$  cluster (AEA = 1.312 eV). Indeed, as indicated by the localization of the singly occupied molecular orbital, the additional electron is in the vicinity of the  $BMg_3$  species (as depicted in Fig. 11). The part of the excess electron density gets transferred to the  $CO_2$  subunit as the initially distant  $CO_2$  approaches  $BMg_3$  to form the  $[BMg_3]^+[CO_2]^-$  ionic system (see Fig. 11 where



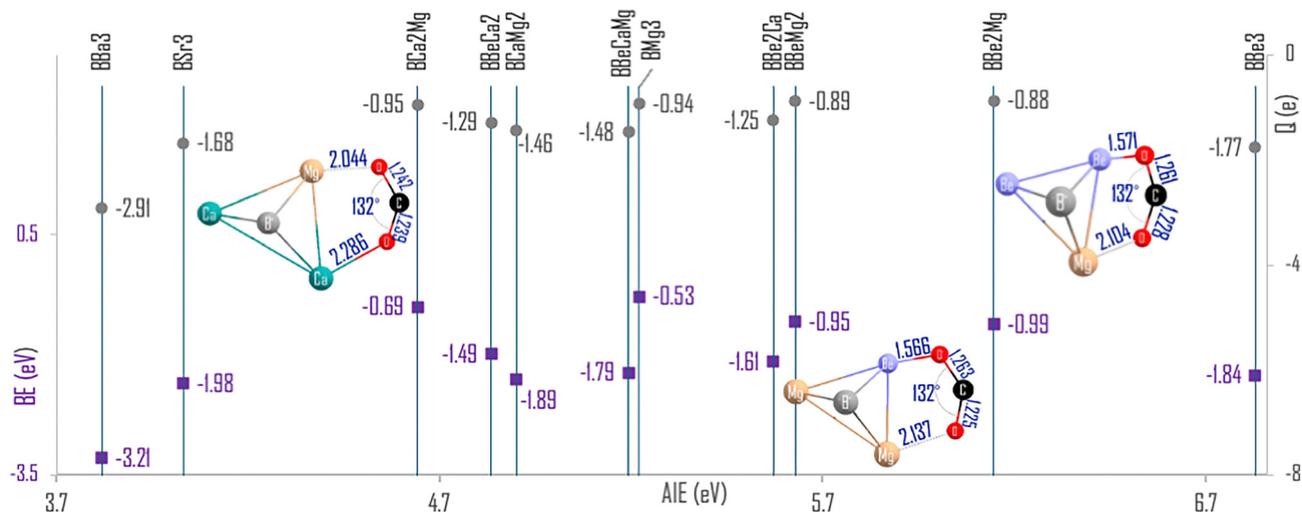


Fig. 9 The influence of the adiabatic ionization energy (AIE, in eV) on the binding energy (BE in eV) and charge flow ( $Q_{\text{CO}_2}^{\text{NBO}}$ ) between the superalkali and  $\text{CO}_2$ . The ground states of representative magnesium-based complexes (*i.e.*,  $\text{BCa}_2\text{Mg}/\text{CO}_2$ ,  $\text{BBaMg}_2/\text{CO}_2$ , and  $\text{BBa}_2\text{Mg}/\text{CO}_2$ ) are also provided.

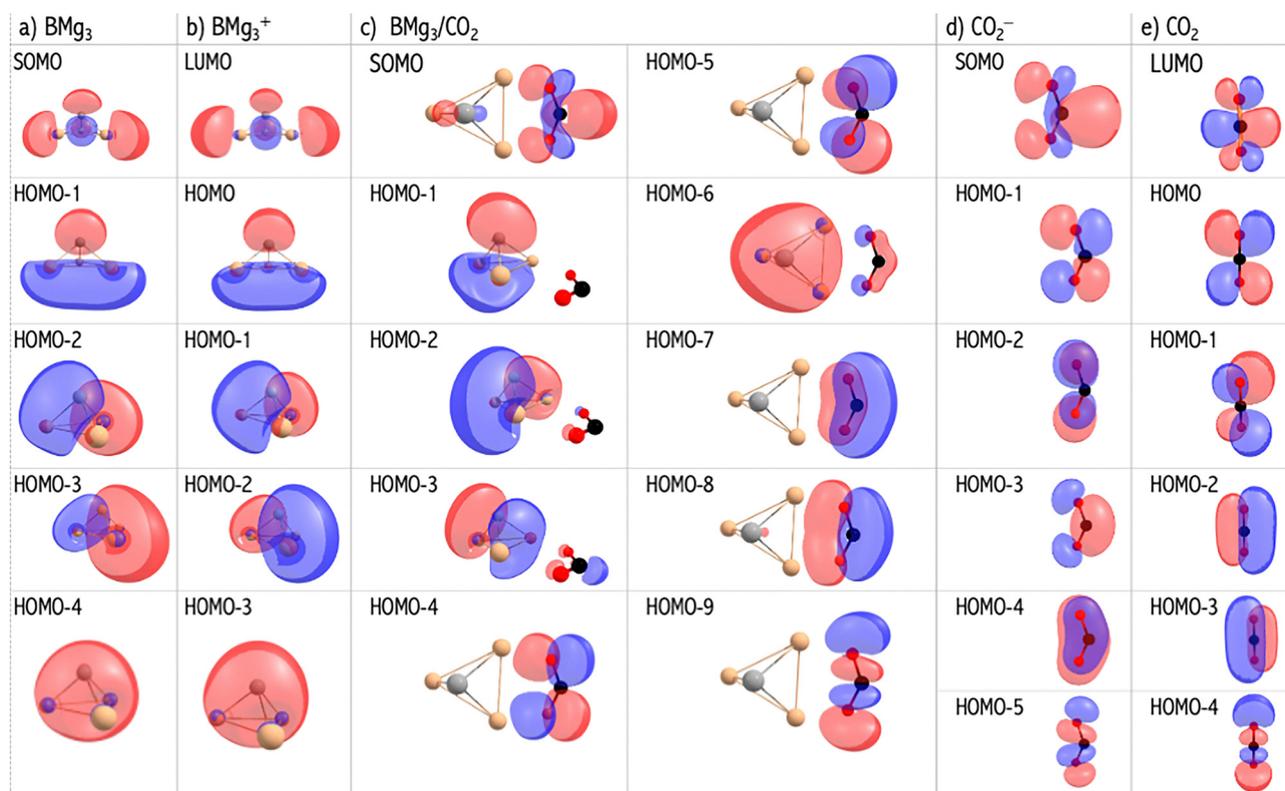


Fig. 10 The molecular orbitals of (a) the  $\text{BMg}_3$  cluster, (b)  $\text{BMg}_3^+$  cation, (c)  $\text{BMg}_3/\text{CO}_2$  compound, (d)  $\text{CO}_2^-$  anion, and (e)  $\text{CO}_2$  molecule. The complete active space self-consistent field method (CASSCF) was used to obtain molecular electronic structures.

also the SOMOs for the equilibrium  $[\text{BMg}_3]^+[\text{CO}_2]^-$  structures are shown). The energy gradually decreases as the  $\text{CO}_2$  molecule approaches the neutral  $\text{BMg}_3$  cluster and there is no barrier that must be surmounted. Such barrierless behaviour is characteristic of gas-phase reactions involving radical species, where long-range capture interactions dominate the dynamics.<sup>63</sup> Since the energy of the separated  $\text{BMg}_3$  radical and  $\text{CO}_2$  molecule is significantly larger

(by *ca.* 0.54 eV) than the energy of the  $[\text{BMg}_3]^+[\text{CO}_2]^-$  ground state, and given that the  $\text{BMg}_3 + \text{CO}_2 \rightarrow [\text{BMg}_3]^+[\text{CO}_2]^-$  process is predicted to be barrier-free, one may expect the  $[\text{BMg}_3]^+[\text{CO}_2]^-$  ionic system to be created spontaneously in the gas phase (whenever  $\text{CO}_2$  molecules find themselves in the vicinity of  $\text{BMg}_3$  clusters).

The above observation implies that the strong reducing ability of a superalkali system makes it possible to activate



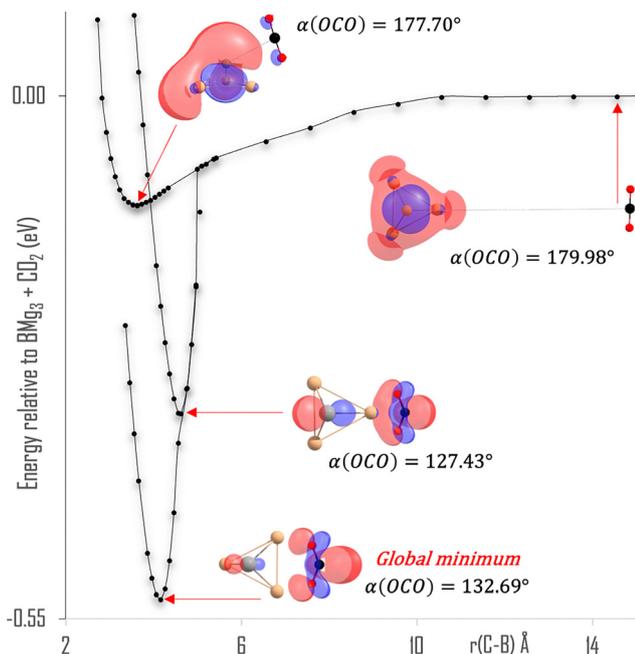


Fig. 11 The CCSD(T)/6-311++G(3df,3pd) energy profiles for the formation of the  $[\text{BMg}_3]^+[\text{CO}_2]^-$  compound according to the  $\text{BMg}_3 + \text{CO}_2 \rightarrow [\text{BMg}_3]^+[\text{CO}_2]^-$  reaction. The relative energies are obtained in relevance to the sum of energies of isolated fragments  $[\text{BMg}_3; \text{CO}_2]$ . The singly occupied molecular orbitals (SOMOs) holding the excess electron are depicted for the structures corresponding to  $r = 4.060$  Å (global minimum),  $r = 4.564$  Å (local minimum), and  $r = 14.564$  Å.

carbon dioxide by electron density transfer from a  $\text{BAe}_3$  cluster to the  $\text{CO}_2$  molecule and form its anionic  $\text{CO}_2^-$  form. Moreover, the binding strength can be modulated by the alkaline earth metal substitution in the  $\text{BAe}_3$  cluster (Fig. 9). The precise control of the binding strength of the carbon dioxide on a molecular cluster is essential for its subsequent transformation into valuable chemicals.

### 3.12. $\text{BAe}_3$ clusters as reducing agents for nitrogen activation

To further testify to the chemical applicability of the designed molecular clusters, the nitrogen molecule activation was investigated. Fig. 12 illustrates the equilibrium geometries of the  $\text{BAe}_3/\text{N}_2$  systems. The comparable energy of the two geometrically stable  $\text{BMg}_3/\text{N}_2$  isomers (*i.e.*, not exceeding 0.1 eV) and the relatively long lifetime of the  $\text{BMg}_3/\text{N}_2$  local minimum ( $\tau = 62.63$  s, see Section S13 in the SI) indicate that the interchange between these structures is probably rapid at the temperatures used experimentally. The binding energy of the  $\text{BAe}_3/\text{N}_2$  ground states was calculated to span the range from  $-0.02$  eV ( $\text{BMg}_3/\text{N}_2$ ) to  $-1.92$  eV ( $\text{BCa}_3/\text{N}_2$ ), and the  $\text{N}_2$  activation process seems to be an exothermic process for all systems. The  $\text{BBe}_3$ ,  $\text{BMg}_3$ , and  $\text{BSr}_3$  non-mixed and  $\text{BCaMg}_2$  and  $\text{BBeCa}_2$  mixed clusters form stable  $[\text{BAe}_3][\text{N}_2]$  complexes in which  $\text{N}_2$  and pyramidal-like  $\text{BAe}_3$  subunits can be distinguished. In turn, the remaining  $\text{BAe}_3$  clusters form strongly bound  $\text{BAe}_3\text{N}_2$  compounds in which the pyramidal-like geometry of the  $\text{BAe}_3$  cluster has not been preserved. While  $\text{BCa}_3/\text{N}_2$  was computed at the  $\text{PBE0}/6-311+\text{G}(3\text{df})$

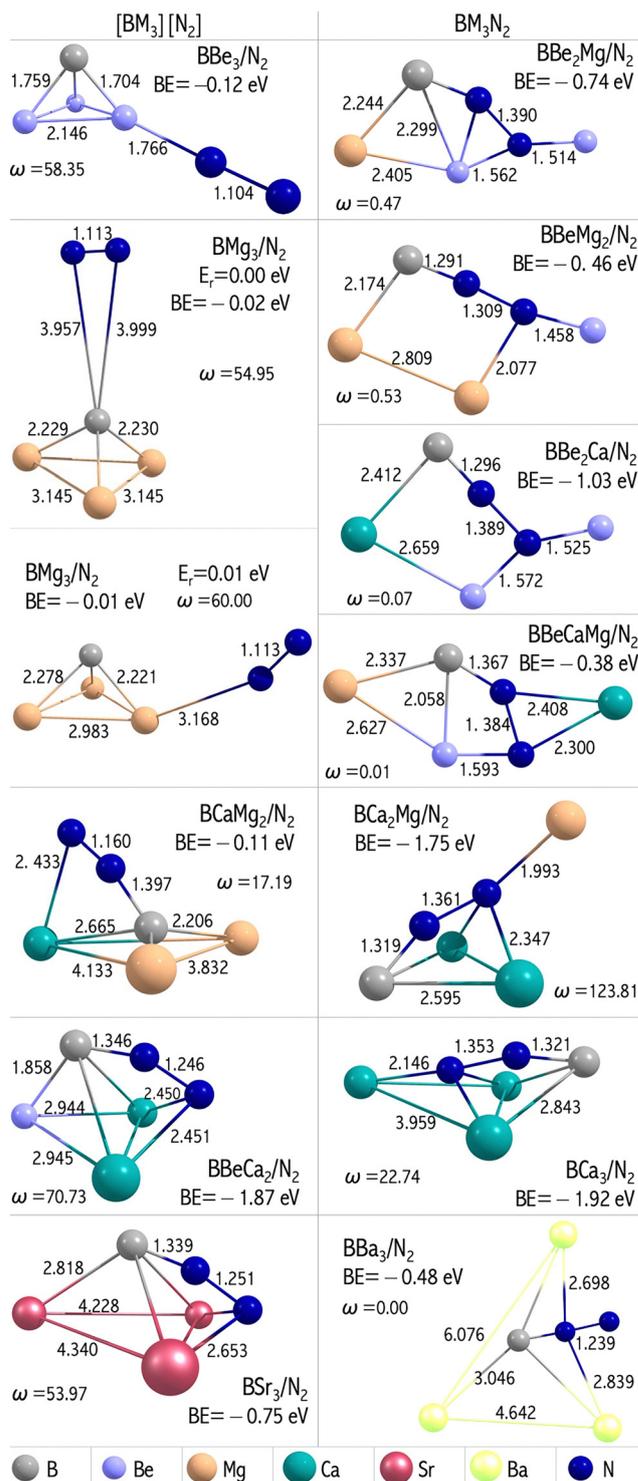


Fig. 12 The MP2/6-311+G(3df)+Def2TZVP ground states of  $[\text{BAe}_3][\text{N}_2]$  and  $\text{BAe}_3\text{N}_2$  ( $\text{Ae} = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{and Ba}$ ) systems. The CCSD(T)/6-311+G(3df)+Def2TZVP//MP2/6-311+G(3df)+Def2TZVP binding energy (BE, in eV). Bond lengths in Å and diedral B-Ae<sub>1</sub>-Ae<sub>2</sub>-Ae<sub>3</sub> angles ( $\omega$ ) in degrees. See Section S12 in the SI for higher energy isomers.

level to be a pyramidal-like  $\text{BCa}_3$  structure linked with a  $\text{N}_2$  molecule through four Ca-N bonds and one B-N *via* an end-on pattern,<sup>35</sup> the calculations at the MP2(full)/6-311+G(3df) level



instead show a planar structure with a bent CO<sub>2</sub> structure inside a triangle formed by three alkaline earth atoms. Like the case in N<sub>4</sub>Mg<sub>6</sub>M/N<sub>2</sub>,<sup>17</sup> the stability of BAe<sub>3</sub>/N<sub>2</sub> (Ae = Be, Mg, and Sr) continuously increases, accompanied by the enhancement of the reducing strength of the non-mixed superalkali cluster. Additionally, the interaction strength depends on the superalkali cluster size. In smaller clusters (such as BMg<sub>3</sub>), the outermost electron is more tightly bound by the nuclei, giving rise to lower reactivity of the cluster (BE = -0.02 eV). The interaction energy increase is naturally accompanied by enhanced charge transfer between the superalkali and N<sub>2</sub> subunits. As shown in Fig. 12, the largest charge flow (of 2.75e) has been observed for the strongest bound BCa<sub>3</sub>/N<sub>2</sub> compound (BE = -1.92 eV). Remarkably, the N-N bond elongates from 1.113 Å (N<sub>2</sub> isolated neutral molecule) up to 1.389 Å (Fig. 12) upon the interaction with the BAe<sub>3</sub> cluster, exhibiting its anionic form. Upon nitrogen gaining one or two electrons, the N-N bond elongates from 1.113 Å (N<sub>2</sub> singlet spin state) to 1.192 Å (N<sub>2</sub><sup>-</sup>) or 1.225 Å (N<sub>2</sub><sup>2-</sup> triplet spin state), respectively, as obtained at the MP2/6-311+G(3df) level. The relatively low second ionization energy of the BAe<sub>3</sub> cluster (AIE2 in Fig. 14a) makes it possible to transfer two electrons from the superalkali to the nitrogen molecule. Consequently, in all BAe<sub>3</sub>N<sub>2</sub> compounds, N<sub>2</sub> is in its dianionic state, which is confirmed by the NBO charge on the N<sub>2</sub> fragment (Fig. 14c) and N-N distances (Fig. 12). The above observation implies that the BAe<sub>3</sub> clusters have a strong reducing ability and can be used for nitrogen molecule activation.

The reduction of the nitrogen molecule by a superalkali has been assessed for an arbitrarily chosen BSr<sub>3</sub>/N<sub>2</sub> system. While analyzing the counterpoise-corrected energy profile for the BSr<sub>3</sub> + N<sub>2</sub> → [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> process, the excess electron is in the vicinity of the BSr<sub>3</sub> species (as depicted in Fig. 13). The part of the excess electron density gets transferred to the N<sub>2</sub> subunit as the initially distant nitrogen molecule approaches the BSr<sub>3</sub> superalkali to form the [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> ionic system (see Fig. 13 where also the SOMOs for the equilibrium [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> structures are shown). The BSr<sub>3</sub>/N<sub>2</sub> system undergoes a decrease in energy as the fragments come together into the [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> ground state. However, upon nearing each other, the system temporarily stabilizes at a local minimum, characterized by a higher energy (by 0.357 eV) than that of the isolated fragments. This suggests that the fragments are interacting but not in the most stable configuration. Due to a sufficiently long lifetime (of 4.88 s, see Section S13 in the SI), the BSr<sub>3</sub>/N<sub>2</sub> local minimum can serve as a metastable trap for intermediates under standard conditions used in the simulations (gas phase and room temperature). As the reaction progresses, the system continues to evolve, eventually reaching the global minimum of 2.191 eV lower in energy than the isolated fragments. The global minimum represents the most stable and energetically favourable state, with the local minimum acting as an intermediate step along the reaction path.

The variation tendency of the regulation effect of the alkaline earth metal atoms on the BAe<sub>3</sub>/N<sub>2</sub> reaction products can relate to the change of the dipole moment ( $\mu$ ) upon the metal atom substitution, with a larger dipole moment promoting the reactivity of a BAe<sub>3</sub> cluster and forming stable, strongly bound

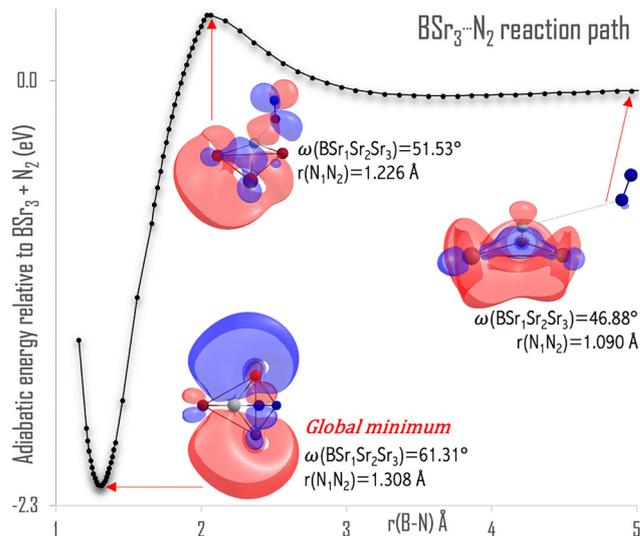


Fig. 13 The BSSE-corrected adiabatic energy profiles for the formation of the [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> compound according to the BSr<sub>3</sub> + N<sub>2</sub> → [BSr<sub>3</sub>]<sup>+</sup>[N<sub>2</sub>]<sup>-</sup> reaction. The relative energies are obtained in relevance to the sum of energies of isolated fragments [BSr<sub>3</sub>, N<sub>2</sub>]. The singly occupied molecular orbitals (SOMOs) holding the excess electron are depicted for the structures corresponding to  $r = 1.302$  Å (global minimum),  $r = 1.965$  Å (local minimum), and  $r = 4.965$  Å. The basis set superposition error (BSSE) has been accounted for by using the counterpoise correction method.

BAe<sub>3</sub>N<sub>2</sub> compounds. Hence, as shown in Fig. 14b, the variation trend of the dipole moments of the BAe<sub>3</sub> clusters agrees with that of the interaction energies for the BAe<sub>3</sub>/N<sub>2</sub> systems. The dipole moment of the molecular cluster can be considered as one signature of reduced stability and enhanced reactivity. As illustrated in Fig. 14b, the BBaCaMg/N<sub>2</sub> ( $\mu = 3.03$  Debye) species is more stable (BE = -0.38 eV) than its neighbouring species, *i.e.*, BMg<sub>3</sub>/N<sub>2</sub> ( $\mu = 1.80$  Debye, BE = -0.02) and BCaMg<sub>2</sub>/N<sub>2</sub> ( $\mu = 1.88$  Debye, BE = -0.11 eV). Such a result of the dipole moment is also consistent with the calculated charge flow ( $Q_{N_2}^{NBO}$ ) values (Fig. 14c). Thus, the above findings demonstrate that the properly chosen BAe<sub>3</sub> clusters can significantly enhance the stability of BAe<sub>3</sub>/N<sub>2</sub> species to transform the N<sub>2</sub> molecule into its activated ionic form.

The interaction of BAe<sub>3</sub> clusters with the N<sub>2</sub> molecule is characterized by the charge transfer from the BAe<sub>3</sub> superalkali to N<sub>2</sub>, resulting in the formation of [superalkali][N<sub>2</sub>] complexes. For example, the N<sub>2</sub> molecule interacts with the N<sub>4</sub>Mg<sub>6</sub>M (M = Li, Na, and K) superalkalis, forming complexes with binding energies of approximately 0.04 to 0.11 eV, accompanied by hardly any charge flow between interacting subunits ( $Q_{N_2}^{NPA}$  up to 0.02e). Utilizing stronger reducing agents (whose ionization energies diminish by 4.4 eV) allowed us to reduce the nitrogen molecule. The nitrogen molecule activation was possible by the low ionization energy of the BAe<sub>3</sub> superalkali, with a smaller ionization energy promoting the transfer of an electron to N<sub>2</sub>. The  $Q_{N_2}^{NPA}$  of BSr<sub>3</sub>/N<sub>2</sub> reads 0.75e which exceeds those gained by N<sub>2</sub> from N<sub>4</sub>Mg<sub>6</sub>Li (0.02e),<sup>17</sup> N<sub>4</sub>Mg<sub>6</sub>Na (0.02e),<sup>17</sup> N<sub>4</sub>Mg<sub>6</sub>K (0.02e),<sup>17</sup> NLi<sub>4</sub> (0.02e),<sup>64</sup> OLi<sub>3</sub> (0.01e),<sup>64</sup> and FLi<sub>2</sub> (0.7e).<sup>64</sup> The transition metal nitride complexes



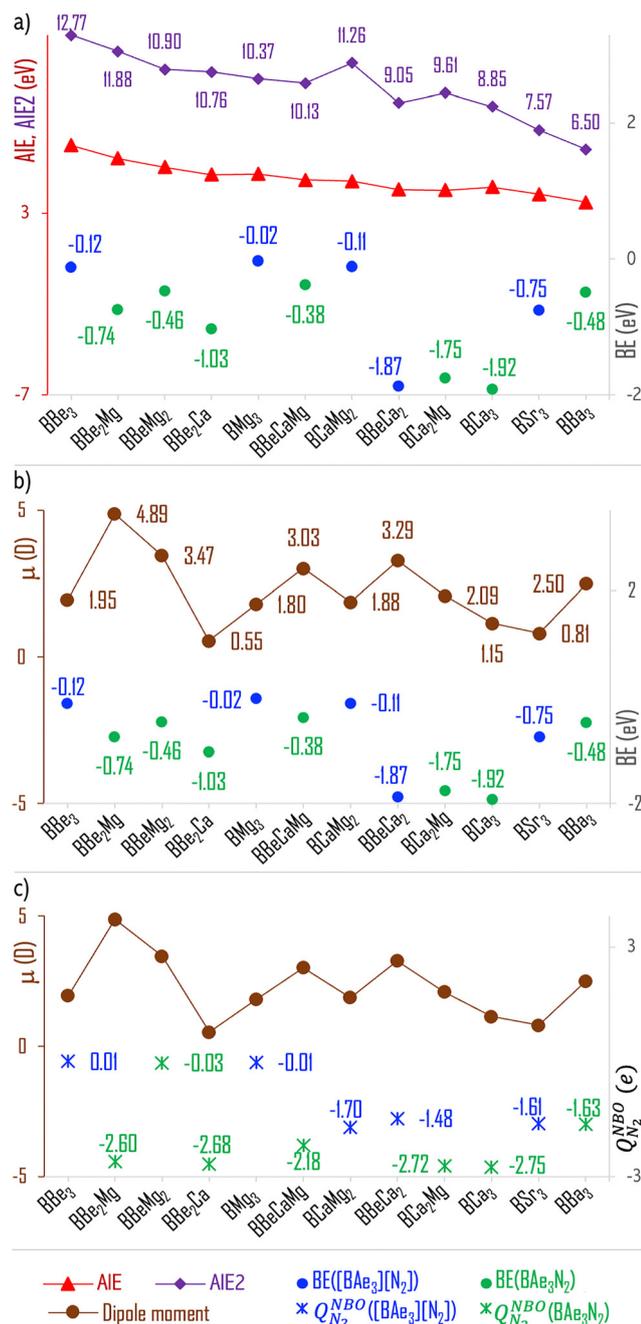


Fig. 14 The first adiabatic ionization energy (AIE, in red), the second adiabatic ionization energy (AIE2, in purple), and dipole moment ( $\mu$ , in Debye) of BAE<sub>3</sub> clusters. (a) and (b) Binding energy (BE, in eV) of [BAe<sub>3</sub>][N<sub>2</sub>] (blue circles) and BAe<sub>3</sub>N<sub>2</sub> (green circles) species. (c) Charge on N<sub>2</sub> by NBO analysis ( $Q_{N_2}^{NBO}$ , in e) of [BAe<sub>3</sub>][N<sub>2</sub>] (blue stars) and BAe<sub>3</sub>N<sub>2</sub> (green stars) species. The BAE<sub>3</sub>/N<sub>2</sub> systems have been sorted by ascending molecular mass of the BAE<sub>3</sub> subunits.

can activate N<sub>2</sub> through electron donation, leading to bond scission.<sup>65</sup> However, they often require high temperatures or pressures for activation. Electrochemical systems activate N<sub>2</sub> by transferring electrons at electrode surfaces. Yet, they may face efficiency challenges, including sluggish kinetics and high energy barriers. The BAE<sub>3</sub> superalkalis, such as BSr<sub>3</sub>, offer a distinct

advantage by facilitating N<sub>2</sub> activation under milder conditions, owing to their unique electronic structures and low ionization energies, which promote effective charge transfer without necessitating extreme conditions.

The BAE<sub>3</sub> clusters possess excellent reducibility and can serve as catalysts. Good catalysts adsorb the reactants strongly enough for them to react but should not bind products permanently. Therefore, we consider the above results on the BAE<sub>3</sub>/CO<sub>2</sub> and BAE<sub>3</sub>/N<sub>2</sub> formation and stability as the first step for the further CO<sub>2</sub> and N<sub>2</sub> transformation into valuable chemicals (such as formic acid, formaldehyde, methanol, or ammonia, respectively). Based on *ab initio* computations, we demonstrated that the reducing ability and reactivity of the BAE<sub>3</sub> clusters can be tuned upon even single atom substitution within the cluster. The ionization energy of the BAE<sub>3</sub> clusters can be precisely controlled by properly chosen alkaline earth metal substituents and predicted from the QSPR model. The suitable electropositive metals with which the central boron atom is decorated can regulate the electronic properties of molecular clusters forming the superalkali. These findings prove that superalkali's properties can be modulated by substituting a single atom within it.

### 3.13. Catalytic potential – future research

The designed BAE<sub>3</sub> clusters, composed of only four atoms, may have reduced capacity to stabilize certain intermediates compared to larger catalysts. However, their unique electronic properties can be advantageous in specific catalytic applications. Recent studies have demonstrated that small metal clusters, such as those composed of platinum, can efficiently catalyze multi-step reactions.<sup>66</sup> For instance, a study involving fully exposed platinum clusters consisting of an average of four platinum atoms supported on nanodiamond@graphene exhibited excellent catalytic performance, highlighting the efficiency of small clusters in facilitating complex catalytic processes. Therefore, while the small size of BAE<sub>3</sub> clusters may influence their ability to stabilize certain intermediates, their distinctive properties could make them suitable for specific catalytic applications. Further computational and experimental investigations are warranted to fully understand their catalytic potential and to explore their effectiveness in various catalytic processes.

Superalkali clusters can interact with CO<sub>2</sub> and N<sub>2</sub> molecules by donating electrons, which is crucial in electrochemical CO<sub>2</sub> and N<sub>2</sub> reduction. The small size of molecular clusters creates a high density of active sites, which can weaken the C=O and N≡N bonds, making it easier for subsequent steps to occur. Our results are the first step for the BAE<sub>3</sub> clusters' catalytic potential assessment. The next step is to investigate their immobilization on the support. Recently, Huang *et al.*<sup>67</sup> described the catalytic activity of Au<sub>25</sub> superatoms immobilized on cerium oxide (CeO<sub>2</sub>) nanorods for styrene activation. They demonstrated that superatomic clusters immobilized on the CeO<sub>2</sub> nanorods maintain the structural and electronic properties of isolated superatoms. Charge transfer from superatoms to CeO<sub>2</sub> affects the charge distribution of the superatom, which may impact the activation of the oxidant on the superatom and bring about different catalytic selectivities. Future studies on



the catalytic potential of  $\text{BAe}_3$  superatoms will at least include superalkali's immobilization on an oxide support (such as  $\text{CeO}_2$  and  $\text{MgO}$ ). Investigation of the structural and electronic stability of  $\text{BAe}_3$  clusters supported on the surface of oxides will allow us to infer the catalytic mechanism and selectivity towards  $\text{CO}_2$  and  $\text{N}_2$ . These future studies will be crucial in understanding the catalytic mechanism of carbon dioxide and nitrogen reduction, as well as correlating the structural information with catalytic features.

## 4. Summary

Based on a hybrid QM-QSPR approach, non-mixed and mixed alkaline earth metal systems were proposed here to demonstrate the ability to regulate the electronic properties of a molecular cluster in rationally designing the highly electropositive species, the superalkali. Different from the conventional formulation-assisted methodology, the QSPR strategy predicts the reducing ability of the superalkali, where a suitable alkaline earth metal increases the ionization energy of the resulting  $\text{BAe}_3$  cluster *via* the B–Ae and Ae–Ae electrostatic effects. It was observed that the increment of the AIE values of the cluster originates from the sum of the first ionization energies of the constituting atoms, and the alkaline earth metal substitution possesses an intriguing power to modulate the electronic properties of the cluster precisely. Apart from the thermodynamic and electronic stability analysis, the reducing ability of the  $\text{BAe}_3$  species was further proved in an interaction with the  $\text{CO}_2$  and  $\text{N}_2$  systems. We demonstrated that the linear carbon dioxide molecule can be effectively reduced to its anionic bent form by utilizing  $\text{BAe}_3$  clusters as reducing agents. From the analysis of the binding energy, the charge transfer, and the geometry of  $\text{BAe}_3/\text{N}_2$  systems, it follows that the resulting structures can be considered as either the  $[\text{BAe}_3][\text{N}_2]$  complexes or the  $\text{BAe}_3\text{N}_2$  compounds. We demonstrated that the ionization energy and the dipole moment of the  $\text{BAe}_3$  clusters determine the stability and geometry of the resulting  $\text{BAe}_3/\text{N}_2$  species. The lower ionization energy and larger dipole moment promote the reactivity of the  $\text{BAe}_3$  cluster and form stable, strongly bound compounds. Our results emphasize how the structure and stability of the  $\text{BAe}_3/\text{N}_2$  systems can be tuned upon single atom substitution. All these findings provide new insights into superalkali design, and we hope the QM-QSPR approach highlighted here can stimulate more efforts from both theorists and experimentalists in designing and synthesizing more superalkalis, which can serve as reducing agents in chemical processes.

## Author contributions

Natalia Wiszowska: investigation, visualization, and writing – review & editing. Natalia Rogoża: investigation, visualization, and writing – review & editing. Celina Sikorska: conceptualization, supervision, writing – original draft, writing – review & editing, and funding acquisition.

## Conflicts of interest

The author declares no conflict of interest.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: molecular coordinates, lower energy isomers, theory level comparison, thermodynamic stability analysis, mathematical model equations, and QSPR modeling details. See DOI: <https://doi.org/10.1039/d5cp02913a>.

## Acknowledgements

This research is part of the project no. 2022/45/P/ST4/01907 co-funded by the National Science Centre and the European Union Framework Programme for Research and Innovation Horizon 2020 under the Marie Skłodowska-Curie grant agreement no. 945339. For the purpose of open access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission. Calculations have been carried out in (a) the Wrocław Centre for Networking and Supercomputing (<https://www.wcss.pl>, grant no. 378), (b) the Centre of Informatics–Tricity Academic Supercomputer and Network (CI TASK) in Gdansk (project no. pt01088), and (c) the New Zealand eScience Infrastructure (NeSI) high-performance computing facilities funded jointly by NeSI's collaborator institutions and through the Ministry of Business, Innovation & Employment's Research Infrastructure program (<https://www.nesi.org.nz>, project no. uoa02699). Celina Sikorska would also like to acknowledge support from the Marsden Fund Council from Government Funding administered by the Royal Society of New Zealand (MFP-21-UOA-069). CS would like to express the deepest gratitude to Prof. Adam Liwo for their outstanding mentorship and support throughout this Polonez Bis project.

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